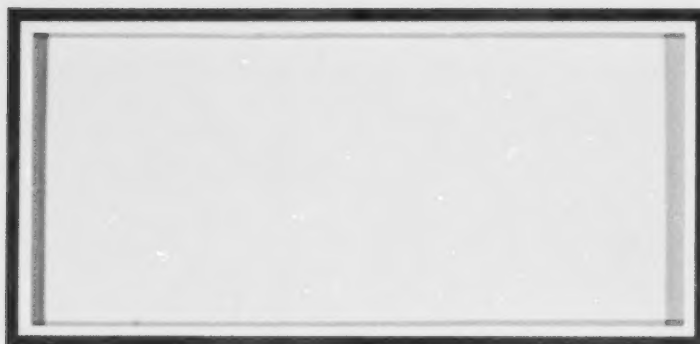




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PHASE I

Preparation of Durable Ceramic Coatings
by Spray Pyrolysis

FINAL REPORT

by

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SUMMARY

The feasibility of producing abrasion resistant coatings, such as Al_2O_3 and ZrO_2 by the spray pyrolysis technique was investigated. It was found that adhesive transparent crystalline zirconia as well as transparent titania coatings from metal alkoxides could be deposited on glass substrates using the spray pyrolysis facility at the Ontario Research Foundation.

It was found that alumina coatings deposited from solutions of inorganic compounds and alkoxides showed poor adherence and had a powdery appearance. A thermodynamic analysis was carried out to investigate the conditions suitable for the deposition of alumina coatings. Temperature and atmospheric humidity appeared to be major factors controlling coating formation.

Transparent ZrO_2 films have successfully been produced by spray pyrolysis of N-Butyl Zirconate on glass substrates. Further coating evaluation and the use of steel and enamelled steel substrates are currently being investigated. Recommendations for the direction of work in Phase II are presented.

1. INTRODUCTION

High wear-resistant ceramic coatings are of great importance to several Canadian industries in a variety of applications ranging from aircraft parts to durable coatings on glass containers using a variety of coating techniques.

On September 21, 1983, the Ontario Research Foundation embarked on a research and development project under the unsolicited proposal program of the Department of Supply and Services with sponsorship by the Department of Energy, Mines and Resources.

The purpose of the program was to demonstrate the feasibility of depositing abrasion resistant coatings using the spray pyrolysis technique, a process readily scaled up to industrial production.

This program is to be carried out in two phases. Phase I of the program involves demonstrating the feasibility of producing abrasion resistant coatings by the spray pyrolysis technique. After feasibility has been demonstrated the deposition of these coatings on industrial useful substrates will be addressed in Phase II.

This interim report, covering the nine month period of Phase I, summarizes the experimental results. An extensive literature survey of spray pyrolysis technology for the deposition of abrasion resistant ceramic coatings is included with the report.

2. OBJECTIVES AND MAJOR TASKS

The purpose of Phase I of the DSS Spray Pyrolysis program which was carried out between September 21, 1982 and June 30, 1983 is to demonstrate the feasibility of producing abrasion resistant coatings by the spray pyrolysis technique.

The specific objectives of this program are:

- (i) To develop a method for the application of abrasion resistant coatings using the spray pyrolysis technique.
- (ii) To evaluate the coatings produced by the spray pyrolysis technique for increasing the abrasion resistance.
- (iii) To assess the industrial potential of abrasion resistant coatings produced by the spray pyrolysis technique.

Phase I of this program consists of the following major tasks:

1. A literature survey of the reagents used for film deposition, the methods for substrate preparation, the properties of the coatings (specifically abrasion resistance) and their industrial potential.
2. The selection of coating compositions to be produced by spray pyrolysis.
3. The selection of reagents for the spray solutions.
4. The development of solution formulations.
5. The selection and preparation of substrates for film deposition.
6. The adaptation of the existing spray system and technology at the Ontario Research Foundation to make it compatible with the solutions formulated under 4.

7. The deposition of films using spray technology.
8. The evaluation of the films deposited in terms of adhesion, hardness, abrasion resistance, thickness and microstructure.
9. The parameters modification of the spray pyrolysis process when the coatings examined under 8. show poor characteristics.
10. A critical examination of the results of the investigation in light of published data in a Final Report for Phase I.

The relationship between the major tasks of Phase I of the program is schematically illustrated in Figure 1.

3. LITERATURE SURVEY

An extensive literature survey of abrasion resistant coatings and spray technology in general has been carried out. Specific coatings, SnO_2 , Al_2O_3 and ZrO_2 , preparatory routes, properties and applications were surveyed. The chemistries of tin, aluminum and zirconium compounds were also investigated to enable the compilation of a short list of coating precursors. The literature survey was also conducted to establish initial spray parameters for the spray pyrolysis system. The completed literature survey is attached as Appendix A.

4. EXPERIMENTAL

4.1 Coatings Selection

Spray pyrolysis involves the deposition of a coating from a solution that is sprayed on a heated substrate. The formation of the coating involves the decomposition of the solute which is the coating precursor in close proximity to the substrate and subsequent reaction with the substrate surface, components of the air or the solvent and its breakdown products. Since atmospheric oxygen is more reactive than nitrogen and since water or other oxygen containing solvents are likely involved it was decided to concentrate the efforts on oxide coatings in this program.

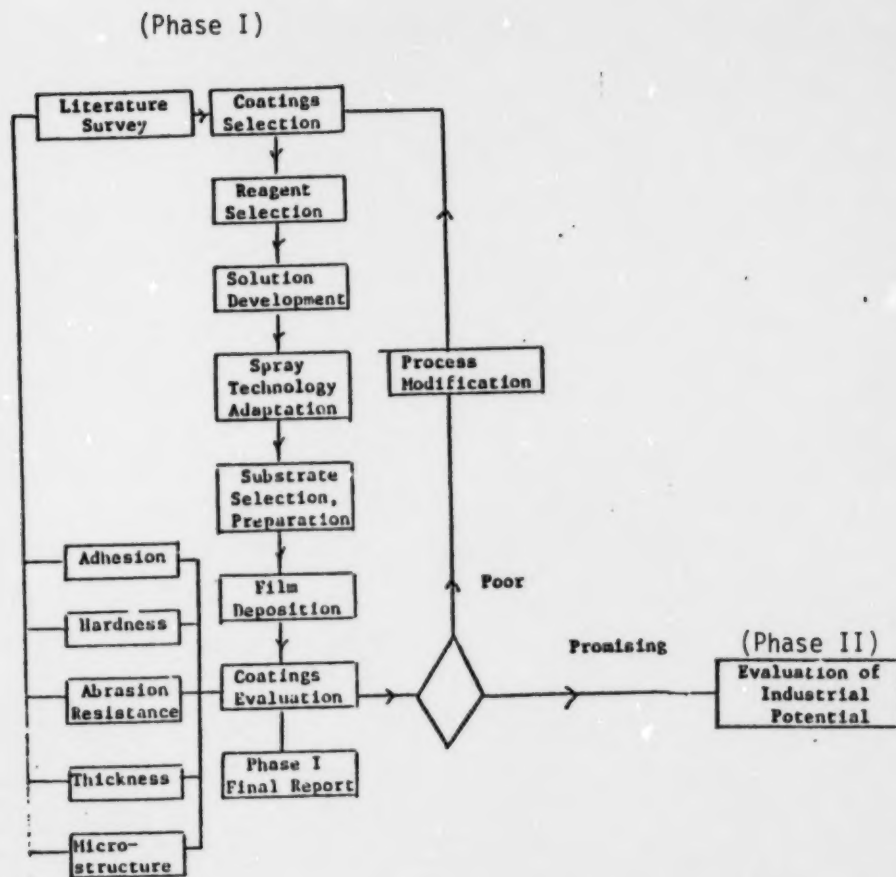


FIGURE 1: RELATIONSHIPS BETWEEN THE MAJOR TASKS (PHASE I) OF THE PROGRAM.

It was decided to investigate simple oxide coatings first since the chemistry of the decomposition-coating formation reaction would be less complicated. Table 1 lists the hardness values for a number of simple binary and ternary materials. It can be seen that the following simple oxides deserve consideration: Al_2O_3 , BeO , ZrO_2 and SiO_2 . BeO was omitted in the selection process because of the known health hazards of beryllium. For the initial investigation, the choice was further narrowed down to Al_2O_3 and ZrO_2 . SnO_2 was added to the short list. Further rationale for the choice of SnO_2 , Al_2O_3 and ZrO_2 is discussed below:

4.1.1 SnO_2

SnO_2 coatings are easily prepared on glass substrates in a simple and industrially developed spray pyrolysis process. Trial runs with SnCl_4 solutions was used to establish initial spray equipment parameters. SnO_2 coatings on glass was used as a reference system for the evaluation of coating performance for other systems.

4.1.2 Al_2O_3

Alumina is a material which is hard, durable and abrasion resistant. Al_2O_3 coatings in combination with TiC have been produced on cemented carbide bits by chemical vapour deposition to improve the tool life.

4.1.3 ZrO_2

Zirconia can be produced in a hard, dense form. Zirconia coatings, stabilized with CaO or Y_2O_3 have been used as thermal barrier coatings for jet engines, etc. These coatings were produced by plasma-arc and related techniques. Although not as hard as alumina, zirconia coatings can be expected to prove extremely useful, especially for high-temperature applications.

4.1.4 Other Coatings

Another oxide coating, TiO_2 , was also investigated briefly as TiO_2 coatings, as well as SnO_2 , are used as hotend coatings for glass bottles to decrease the abrasion damage due to mechanical handling.

TABLE 1

Comparison of Hardness Values of Various
Materials on Mohs and Knoop Scales

Substance	Formula	Mohs value	Knoop value
Talc.....	$3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$	1	
Gypsum.....	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	2	32
Cadmium.....	Cd	..	37
Silver.....	Ag	..	60
Zinc.....	Zn	..	119
Calcite.....	CaCO_3	3	135
Fluorite.....	CaF_2	4	163
Copper.....	Cu	..	163
Magnesia.....	MgO	..	370
Apatite.....	$\text{Ca}_5\text{F}(\text{PO}_4)_3$	5	430
Nickel.....	Ni	..	557
Glass (soda lime).....		..	530
Feldspar (orthoclase).....	$\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$	6	560
Quartz.....	SiO_2	7	820
Chromium.....	Cr	..	935
Zirconia.....	ZrO_2	..	1160
Beryllia.....	BeO	..	1250
Topaz.....	$(\text{AlF})_2\text{SiO}_4$	8	1340
Garnet.....	$\text{Al}_2\text{O}_3 \cdot 3\text{FeO} \cdot 3\text{SiO}_2$	..	1360
Tungsten carbide alloy.....	WC, Co	..	1400-1800
Zirconium boride.....	ZrB_2	..	1550
Titanium nitride.....	TiN	9	1800
Tungsten carbide.....	WC	..	1880
Tantalum carbide.....	TaC	..	2000
Zirconium carbide.....	ZrC	..	2100
Alumina.....	Al_2O_3	..	2100
Beryllium carbide.....	Be_3C	..	2410
Titanium carbide.....	TiC	..	2470
Silicon carbide.....	SiC	..	2480
Aluminum boride.....	AlB	..	2500
Boron carbide.....	B_4C	..	2750
Diamond.....	C	10	7000

* Acknowledgment is made to N. W. Thibault, Norton Company, Worcester, Massachusetts, for many of Knoop hardness values. Cf. R. F. Geller, "A Study of Ceramics for Nuclear Reactors," *Nucleonics*, Vol. 7, No. 4, Table 1, pp. 8-9 (Oct. 1950). V. E. Lysaght, *Indentation Hardness Testing*, Reinhold 1949.

From Ref. 1

Weast, Handbook of Chemistry and Physics 63rd Ed.

4.2 Reagent Selection and Solution Development

Candidate precursors for the deposition of SnO_2 , Al_2O_3 and ZrO_2 coatings, including suitable solvents were selected from data collected in the literature survey. Solutions should be easily produced and chemically stable. Concentration ranges were generally not available and had to be determined by experimentation. The following solute-solvent systems have been investigated to-date:

4.2.1 SnO_2

$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}/\text{water}$

$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}/(\text{water-ethanol})$

4.2.2 Al_2O_3

$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}/\text{water} - \text{ethanol} (50/50)$

$\text{AlCl}_3(\text{anhydrous})/\text{absolute alcohol, benzene, toluene, chloroform, carbon tetrachloride, freon}$

$\text{AlF}_3 \cdot 3\text{H}_2\text{O}$

$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}/\text{water} - \text{ethanol} (50/50)$

$\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}/\text{water}$

$\text{Al}(\text{OR})_3/\text{benzene, toluene, alcohol}$

AlCl_3 and $\text{SnCl}_4/\text{water} - \text{ethanol} (50/50), \text{ethanol}$

Al_2O_3 powder in $\text{SnCl}_4/\text{water} - \text{ethanol} (50/50)$

$\text{Al}(\text{NO}_3)_3$ and $\text{SnCl}_4/\text{water} - \text{ethanol} (50/50)$

4.2.3 ZrO_2

$\text{Zr}(\text{OR})_4/\text{alcohol}$

4.2.4 TiO_2

$\text{Ti}(\text{OR})_4/\text{alcohol}$

4.3 Substrate Selection and Preparation

4.3.1 Substrate Selection

In the initial phase of the program, window glass substrates were used.

Window glass was chosen because:

- 1) it is common and readily available
- 2) it is inexpensive
- 3) it is easy to cut
- 4) it is inert (with respect to oxidation)
- 5) it has higher heat capacity than sheet steel due to greater thickness
- 6) it is an oxide substrate; chemically more compatible with oxide coatings than steel
- 7) it has a thermal expansion coefficient closely matched to that of alumina ($\sim 8 \times 10^{-6}$ cm/cm/K)
- 8) ZnO, SnO₂, In₂O₃ and other coatings have been produced on window glass by spray pyrolysis.

4.3.2 Substrate Preparation

Window glass panels were cut to the size desirable for the spraying trials: 17.7 cm x 10.1 cm. The glass samples were cleaned and rinsed with ethanol and acetone prior to coating deposition.

4.4 The Spray Pyrolysis Set-up at ORF

A description of the spray pyrolysis set-up at ORF is given in Appendix B, attached to this report.

4.5 Spray Technology Adaptation

4.5.1 Substrate Temperature Profile

The substrate in the furnace inside the spraying compartment is originally at the temperature to which it was heated. But it will cool to some extent while lifting out of the furnace and during the spraying

operation. The amount of cooling depends on the thickness and specific heat of the substrate, the spray time and the conditions of the spraying process.

Substrate temperature profiles for window glass substrates were attempted by attaching chromel-alumel thermocouples to the substrate. An infrared pyrometer, IRCON Model 300L was used to record the time temperature profile using an assumed constant sample emissivity.

4.5.2 Spraying Parameters

Spraying parameters to produce uniform and even coatings were established by preparation of SnO_2 coatings on window glass. Those parameters included air pressure, solution flowrate, orifice size of the nozzle, spraying distance, spray cycle, heating times and furnace temperature.

4.6 Film Deposition

SnO_2 , Al_2O_3 , mixed SnO_2 - Al_2O_3 , ZrO_2 and TiO_2 coatings were produced on window glass substrates by spray pyrolysis. The furnace temperatures for the substrate were ranged from 200-850°C.

4.7 Coating Evaluation

Coatings with promising appearance were evaluated using the following methods:

4.7.1 Adhesion

The adhesion test was done by placing a pressure sensitive tape over the film and subsequently removing the tape. This test method is similar to ASTM B-571-72.

4.7.2 Hardness

The microhardness of the coatings was measured with the Knoop indentation technique using a 10g-100g load.

4.7.3 Abrasion Resistance

The abrasion resistance was tested with a sand grit blaster using 5g. of #120 grit SiC with 20 psi blast air pressure for 30 seconds to a 3/8 dia. exposed area. The test method was similar to the ASTM C-158-80 Standard.

4.7.4 Thickness

The film thickness was measured with a Rank-Taylor-Hobson Talysurf-4 and by optical microscopy and scanning electron microscopy. Talysurf-4 thickness measurement did not prove to be successful. Interference colour changes were used to estimate film thickness.

4.7.5 Microstructure

Optical microscopy and scanning electron microscopy (SEM) were used to examine the film morphology.

5. RESULTS AND DISCUSSION

5.1 Apparatus Set-up

5.1.1 Equipment

The computer controlled spray pyrolysis setup at ORF was tested by spraying SnCl_4 solutions on window glass. Test runs showed that the spray setup was working satisfactorily.

5.1.2 Substrate Temperature Profile

For an adherent coating to be formed, the substrate temperature must at least equal the decomposition temperature of the film precursor when the vapour reaches the substrate. Under those conditions, there will be a high probability that the chemical bonds in the precursor molecule will be broken and replaced by bonds between the metal of the coating and substrate atoms.

5.1.2.1 Chromel-Alumel Thermocouple

(a) Window Glass Substrate

Initial experimental work was carried out on window glass substrates. A glass plate was lowered into the furnace at 600°C with

a thermocouple touching the surface of the glass. When the temperature of the glass stabilized, the plate was lifted from the furnace. The temperature profile of the glass was recorded (Appendix C, Figure C1). Apparently, it took 3 minutes for the plate to reach 588°C in the furnace. The temperature of the plate dropped off very rapidly when it was removed from the furnace.

The temperature of the glass was 679°C after 2 min. in the furnace at 850°C (Appendix C, Figure C2). The temperature of the glass dropped rapidly after it was lifted out of the furnace. This temperature and time were determined as being the maximum that a window glass could withstand before deformation occurred.

(b) Steel Substrate

The temperature of the 430 stainless steel was 882°C after 1 min. in the furnace at 1050°C (Appendix C, Figure C3). The temperature of the steel plate dropped more rapidly than that of the window glass.

5.1.2.2 Infrared Pyrometer

An infrared pyrometer (IRCON Model 300L) was used to measure the temperature of the glass surface. The temperature drop of the glass surface was measured before and after spraying. Spraying was carried out for 0, 5, 10, 15 and 20 s. The actual temperatures measured are given in Appendix C, Tables C1 and C2 and Figures C4 and C5.

5.1.3 Spray Parameters

Initial experimental work was carried out on glass substrates with aqueous solutions of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ to produce SnO_2 coatings. Using the existing spray pyrolysis apparatus set-up at ORF, spray parameters and solution parameters that produced coatings with a good appearance were established. The optimum parameters listed in Table 2, can be used as initial spray

parameters for the deposition of Al_2O_3 and ZrO_2 films.

TABLE 2

Optimum Conditions for SnO_2 Coatings on Glass

Furnace Temp.	Furnace Duration	Air Pressure	Solution Flowrate	Orifice Size	Distance to Substrate	Spray Cycle
850°C	2 min.	40 psi	.9 GPH	¼J-2A	18 in.	10 s.

Initial runs in this system showed localized deposits at the central region of the glass substrates and the deposits lacked homogeneity. These deficiencies were overcome by lowering the air pressure from 70 to 40 psi and by increasing the distance between spray gun and substrate surface from 15 to 18 inches.

The use of an on/off rather than a continuous spray cycle eliminated the sputtery appearance of the coatings. Also, coatings showed improved hardness after reheating and respraying.

Detailed results of the spray parameter optimization trials are given in Appendix D, Table D1.

5.2 SnO_2 Coatings on Window Glass Substrates

5.2.1 Solution Development

Experimental work was carried out to determine the solution parameters that enable good SnO_2 coatings to be produced by spray pyrolysis. Aqueous solutions of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ in ethanol/water (50/50) were tested using the existing spray pyrolysis apparatus setup. The parameters that were emphasized were: reagent concentration, pH value, furnace temperature and holding time in the furnace. The reagent concentrations in this series ranged from 0.2M-2.6M, pH values ranged from 0.4 to 0.6 and furnace temperatures and times ranged from 625°C for 5 min. to 1000°C for 1/2 min. For

this series of concentrations, the best parameters for SnO_2 deposition by spray pyrolysis are as follows:

Reagent: Aqueous solution of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ 0.8M

pH value: 0.4

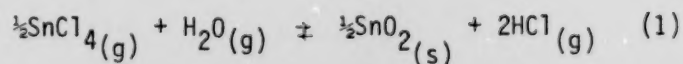
Furnace Temperature & Time: 850°C for 2 min.

Using pressure sensitive tapes, no removal of the coating from the glass was evident. The adhesion of SnO_2 coating on glass produced by spray pyrolysis was excellent. The Knoop hardness test gave a value of 876 KHN compared with a value of 500 KHN for window glass. The detailed results of this series of experiments, see Appendix D, Table D2.

5.2.2 Theoretical Studies of SnO_2 Coatings

5.2.2.1 Thermodynamic Studies on SnCl_4 Oxidation

Aitchison ⁽²⁾ prepared transparent tin oxide film by the hydrolysis of an inorganic halide on a heated substrate. The basic reaction for the formation of tin (IV) oxide is:



The free energy, ΔG° and equilibrium constant K at various temperatures were calculated using Barin and Knache's Tables ⁽³⁾. The results are listed in Table 3.

TABLE 3
 ΔG_T° and K values for reaction (1)

T(K)	ΔG_T° (Kcal)	K
300	-0.335	1.75
500	-2.868	17.9
700	-4.536	26.1
900	-6.384	35.5
795	-5.438	30.6

It can be seen that the reaction is thermodynamically favorable. Figure 2 shows schematically the conditions under which the reaction becomes favorable. The equilibrium constant

$$K = \frac{P_{\text{HCl}}^2}{P_{\text{SnCl}_4}^{1/2} \cdot P_{\text{H}_2\text{O}}} \quad (2)$$

Equation (2) can be rewritten as

$$K \cdot P_{\text{SnCl}_4}^{1/2} = \frac{P_{\text{HCl}}^2}{P_{\text{H}_2\text{O}}} \quad (3)$$

Assuming that $P_{\text{SnCl}_4} = 1$ atm, this equation becomes

$$K' = \frac{P_{\text{HCl}}^2}{P_{\text{H}_2\text{O}}} \quad (4)$$

where K' has numerically the same value as K .

From (4) it follows that

$$\log K' = 2 \log P_{\text{HCl}} - \log P_{\text{H}_2\text{O}} \quad (5)$$

or

$$\log P_{\text{HCl}} = \frac{1}{2} \log K' + \frac{1}{2} \log P_{\text{H}_2\text{O}} \quad (6)$$

The relationship between $\log P_{\text{HCl}}$ and $\log P_{\text{H}_2\text{O}}$ is linear, as evident from Figure 2. Changing P_{SnCl_4} merely shifts the straight line parallel to the position for $P_{\text{SnCl}_4} = 1$ atm.

The curve obtained can be interpreted as follows: Decreasing $P_{\text{H}_2\text{O}}$ shifts the equilibrium (1) to the left hand side, i.e. toward the formation of SnCl_4 . Decreasing the P_{HCl} shifts equilibrium (1) to the right, i.e. toward the formation of SnO_2 . The straight line can be viewed as the boundary where the regions favouring $\text{SnCl}_{4(g)}$ and $\text{SnO}_{2(s)}$ meet. Ideally, spray pyrolysis should take place under conditions where $\text{SnCl}_{4(g)}$ just decomposes to $\text{SnO}_{2(s)}$.

The conditions under which the best SnO_2 coatings were formed have been used to calculate thermodynamic analogies. The average substrate temperature is 522°C or 795 K. Using a 0.8M $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ solution and assuming that all atmospheric gases are displaced by SnCl_4 and H_2O gives $P_{\text{SnCl}_4} \sim 0.01$ atm, $P_{\text{H}_2\text{O}} \sim 1$ atm. Under those conditions P_{HCl} is found to be 1.75 atm. It can be seen that the partial pressures encountered in this experiment are also those that favour the $\text{SnCl}_4 + \text{SnO}_2$ reaction under the conditions of the experiment. A situation where the boundary line would have been much higher (SnO_2 forms too easily) or much lower (SnCl_4 does not react) is unfavourable. Figure 2 also shows how to increase the formation of SnO_2 :

- (a) increase $P_{\text{H}_2\text{O}}$
- (b) decrease P_{HCl}
- (c) increase P_{SnCl_4}
- (d) increase the temperature.

A similar model can be developed for the reaction between tin (IV) chloride and oxygen. This reaction proceeds according to:



Figure 2.

Relationship of P_{H_2O} and P_{HCl} for the Reaction

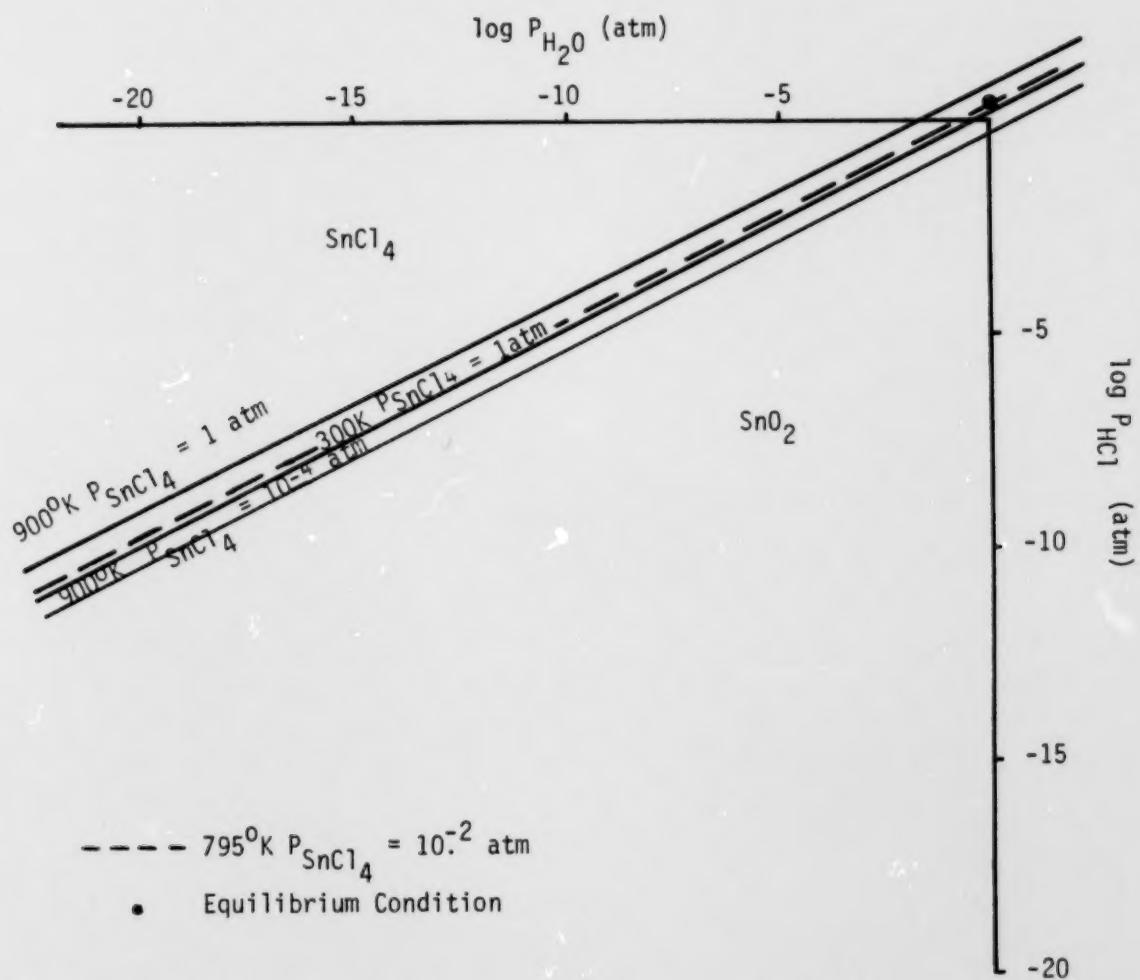


Figure 3 represents the results of the thermodynamic analysis. It can be seen that this reaction is much more favorable for the formation of $\text{SnO}_{2(s)}$ than the reaction with $\text{H}_2\text{O}_{(g)}$. Still, this reaction does not proceed as readily since the reaction is kinetically slow because of the high potential energy barrier.

5.2.2.2 Kinetic Factors

Aitchison (2) also reported that the hydrolysis reaction proceeds very slowly at 500°C and is very rapid at temperatures in the vicinity of 800°C . At a temperature of 1000°C a layer of metallic tin is produced when organic solvents are used. An optimum temperature range is between 500 and 800°C . This reaction normally proceeds very rapidly and is modified by mixing the tin halide with ethanol, acetic acid or a mixture of the two. The breakdown of the organic constituents of the spray introduces reducing conditions and the resulting tin oxide layer is of non-stoichiometric composition if prepared at high temperature.

SnCl_4 forms a stable vapor phase at room temperature (not oxidizing nor hydrolysing in air). It is transported very close to the hot substrate where the reaction will take place.

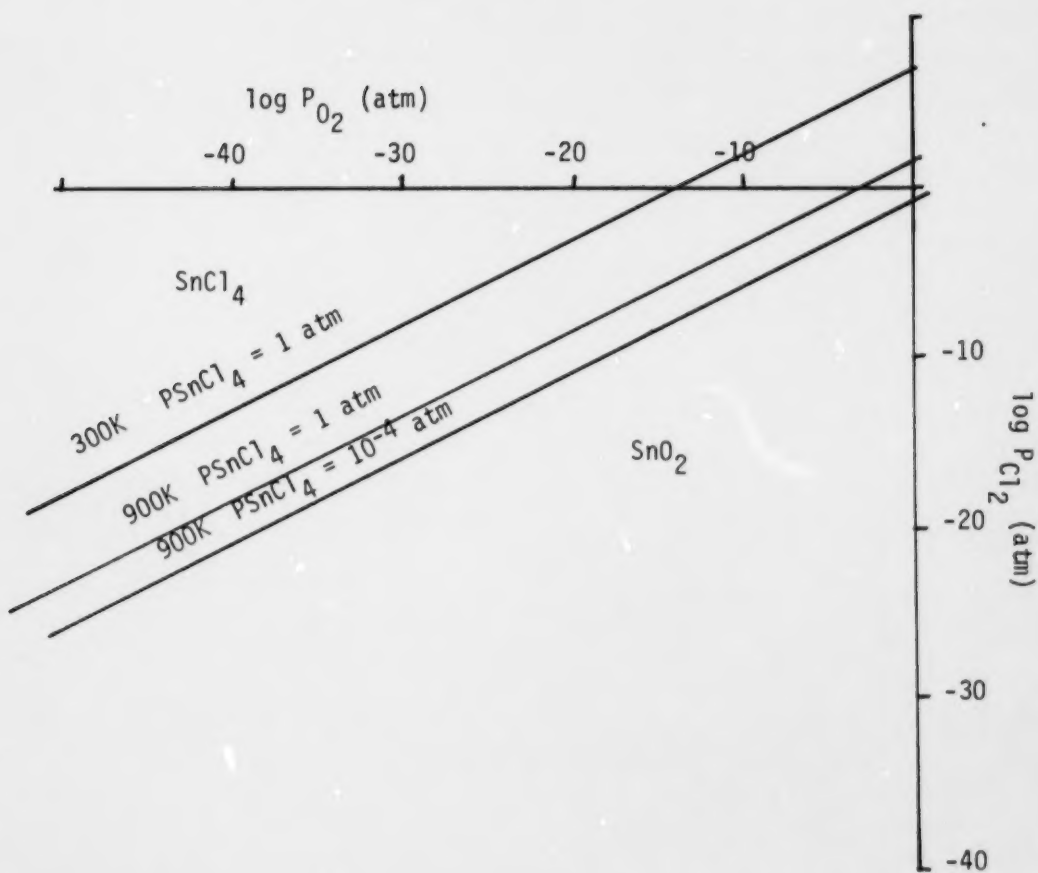
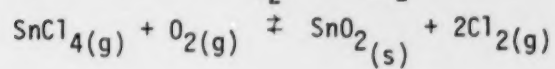
5.2.2.3 Reaction Mechanism

A possible model for the reaction that produces the SnO_2 coating is given in Figure 4.

$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ dissolves in water to give $\text{SnCl}_4(\text{aq})$. The bond energy of Sn-Cl is $344 \text{ kJ} \cdot \text{mol}^{-1}$ (4). No bond energy for Sn-O is given in the literature but on the basis of the similarity in bond energies for Group IV A metal halides ($327\text{--}391 \text{ kJ} \cdot \text{mol}^{-1}$) and C-O ($336 \text{ kJ} \cdot \text{mol}^{-1}$) and Si-O ($368 \text{ kJ} \cdot \text{mol}^{-1}$) (4) it is expected that the Sn-O bond energy will be in the same range and thus be similar to that of Sn-Cl . In solution we expect only partial hydrolysis of the type and no extensive polymerization.

Figure 3.

Relationship of P_{O_2} and P_{Cl_2} for the reaction



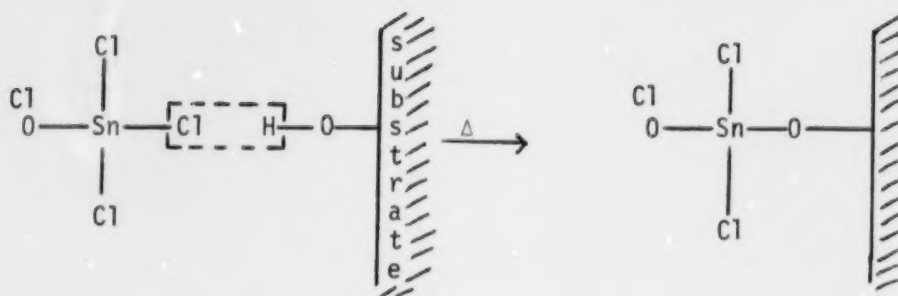
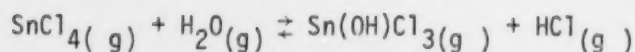
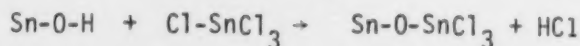


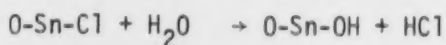
Figure 4. Model for the reaction that produces the SnO_2 coating.



Upon approaching the heated substrate the solvent will evaporate leaving essentially mixed tin(IV) hydroxy chlorides of the type $\text{Sn}(\text{OH})_n\text{Cl}_{4-n}$ ($n = 1-3$). Upon approaching the substrate surface reactions of the type shown in Figure 4 can occur between glass surface hydroxy and tin chloride groups to establish a bond between Sn and the substrate oxygens. The coating is subsequently built up by reactions between adjacent tin configurations of the type:



Water vapor will complete the chloride - hydroxy conversion



The overall reaction is governed by the thermodynamic arguments put forward in Section 5.2.2.1 as well as diffusion and kinetic parameters.

5.3 Al_2O_3 Coatings on Window Glass Substrates

5.3.1 Hydrated Aluminum Chloride

Aqueous solutions of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ in ethanol/water (50/50 by vol) were sprayed in an effort to produce Al_2O_3 coatings. Reagent concentration, pH value, furnace temperature and time were the parameters of main

interest. Initially, the reagent concentrations ranged from 0.2-0.8M; pH values ranged from 1.7-2.2, and furnace temperatures and times ranged from 850°C-825°C for 10-30 seconds for window glass.

All films produced in this series were poor being a non-adherent powder film. Optimum parameters could not be determined. For window glass deposition at high temperature, the coating appeared as loose yellowish powders, while at low temperatures, loose white powders were produced. Coating adhesion was not satisfactory.

In a second set of experiments a 0.8M solution of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ in ethanol/water (50/50) was sprayed on window glass substrates. The furnace temperatures and holding times ranged from 200-850°C and 2-12 min., respectively.

The coatings produced at the lower furnace temperatures of 200-400°C had good overall appearance with limited to poor adhesion. The coating produced was an even, thick white film, smooth and with some adherence but could be removed by scratching. Following heat treatment to 850°C for 90 seconds, the coating became powdery and was easily removed.

Details of the runs can be found in Appendix D, Table D3.

5.3.2 Anhydrous Aluminum Chloride

A 1.9M solution of anhydrous AlCl_3 in absolute alcohol was sprayed on a window glass substrate. The furnace temperatures ranging from 200°C to 650°C were employed. The coating produced was a loose white to beige powdery deposit. The amount of the deposit was reduced as the furnace temperature was raised.

Non-aqueous solutions of anhydrous AlCl_3 saturated in freon, benzene, toluene, chloroform and carbon tetrachloride were sprayed at furnace temperature of 400°C and 650°C. White powder and non-adhesive coatings were formed on the glass. Apparently, anhydrous AlCl_3 hydrolysed in the air and polymerized prior to reaching the glass surface.

Details of the runs are given in Appendix D, Table D4.

5.3.3 Hydrated Aluminum Fluoride

Aluminum chloride (either in the hydrated form in ethanol/water solutions or in the anhydrous form in non-aqueous solvents) appears to form poorly adhesive powdery deposits. A thermodynamic study (see Section 5.3.7) showed that the formation of Al_2O_3 is extremely favourable under the conditions typical of an open spray pyrolysis system.

It is possible that the higher bond energy of the Al-O bond compared to that of the Al-Cl bond could favour the formation of Al_xO_y species. The Al-Cl bond energy is reported to be 418 kJ.mol^{-1} (5). Using Janaf's Thermochemical Tables ⁽¹⁵⁾ we estimated the bond energy of Al-O to be 497 kJ.mol^{-1} by considering the reaction



Thus, the bond energy of the Al-O bond is substantially higher than that of the Al-Cl bond. As a result the formation of Al_2O_3 is extremely favorable when AlCl_3 is the coating precursor.

We have examined several options. One possibility would be to use an aluminum compound Al_pX_q for which the Al-X bond energy is substantially higher than the bond energy of the Al-Cl bond. The Al-F bond energy (581 kJ.mol^{-1}) (5) is substantially higher than that of the Al-Cl bond. Candidate compounds are $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$, $\text{AlF}_3 \cdot 6\text{H}_2\text{O}$, $\text{AlF}_3 \cdot 9\text{H}_2\text{O}$. In solutions the hexaquo cation and its derivatives from successive replacement of H_2O by fluoride are present, as well as the anion AlF_4^- . The nonahydrate is reported to be very soluble in water (6).

Since no commercial supplier of $\text{AlF}_3 \cdot 9\text{H}_2\text{O}$ could be found, this route was not pursued further.

5.3.4 Aluminum Nitrate

Another approach is to choose a compound with Al-O bonds rather than Al-Cl bonds. The similarity in Al-O bond energies between the reagent

Al-O species and the Al_2O_3 to be formed can be expected to lead to slower Al_2O_3 formation compared with the reaction pathways using AlCl_3 .

An aqueous solution of 0.60M (20 wt.%) $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in a 50/50 ratio of $\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH}$ (saturated) was prepared and was sprayed on a window glass substrate. The furnace temperatures and holding times ranged from 200°C - 850°C and 2 min-12 min. respectively. The coating with the best appearance was produced by using the following parameters.

Furnace Temperature - $400^\circ\text{C}/2$ min

Spray Cycle - spray: 10 sec, reheat: 90 sec, re-spray: 10 sec.

Detailed results are listed in Appendix D, Table D5.

The coating produced is an even, thick, white film. The adhesion of the coating showed some improvement when compared with the adhesion of a coating produced from an aqueous solution of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$. Instead of being easily brushed away from the surface, the coating sticks onto the glass. But the coating can be removed by scratching or by a pressure sensitive tape.

The nature of the coatings was elucidated by Raman spectroscopy. The Raman spectra of a coating deposited at a substrate temperature of 400°C , $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and Al_2O_3 were compared. Features of the spectra of both compounds were found in the spectrum of the coating. The Raman spectra are attached to this report as Appendix E.

These observations are in agreement with the known thermal behaviour of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Minayama and coworkers⁽⁷⁾ describe the formation of a mixed $\text{Al}_2\text{O}_3 \cdot \text{Al}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ adduct by thermal treatment of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ at 120°C for 15 hours at a pressure of 460 mm Hg. Koemon and Shimizu describe the thermal decomposition of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{OAc})_3$ at temperatures in the 500 - 700°C range, which produces amorphous Al_2O_3 ⁽¹⁸⁾.

5.3.5 Aluminum Sulphate

Aluminum sulphate which also has Al-O bonds can be expected to behave similarly to aluminum nitrate.

To extend the spectrum of inorganic aluminum salts, a 20 wt.% solution of $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ was sprayed onto window glass substrates. A furnace temperature range of 200-800°C was investigated. A non-adhesive white powder was formed between 600 and 800°C.

Coatings on substrates which had been held at furnace temperatures between 200 and 250°C showed good adhesion and were semi-transparent. Some of the coatings showed a central region which was transparent.

These coatings were subsequently heat treated at different temperatures (500-1000°C for 8-1 minutes) to convert the remaining $\text{Al}_2(\text{SO}_4)_3$ of the deposits to Al_2O_3 . Such a heat treatment yielded a white non-adhesive powder. The microhardness values of the coatings were low (due to poor adhesion), although higher heat treatment temperature (from 500 to 1000°C) increased the Knoop hardness value from 253 to 470. Base glass hardness values of ~ 500 were measured on the back side of the sample.

Detailed results of these runs are given in Appendix D, Table D6.

5.3.6 Aluminum Alkoxides

Aluminum alkoxides were considered as potentially useful reagents for the deposition of alumina films because of the work of Aboaf ⁽⁹⁾ who used thermal decomposition at 420°C of aluminum triisopropoxide, $\text{Al}(\text{OC}_3\text{H}_7)_3$, to produce amorphous aluminum oxide films. The films deposited on germanium or silicon wafers were adherent, transparent and hard.

Aluminum alkoxides hydrolyze easily in air to give $\text{Al}(\text{OH})_3$ and the derived alcohol. Initial attempts to dissolve aluminum triisopropoxide and aluminum-sec butoxide in toluene, benzene, ethanol, propanol or butanol were unsuccessful. In each case, a gel was formed. Clear solutions were obtained, however when the solutions are predried with a molecular sieve. These solutions begin to gel soon after contact with the air.

To limit the hydrolysis of the alkoxide solutions, nitrogen was used for atomization instead of air. With both N_2 and air, the hydrolysis products of the spray solution tended to block the passages in the spray equipment. Better results were obtained when the spray set-up was pre-flushed with pure acetone and toluene to remove the blockages and traces of water.

5.3.6.1 $\text{Al}(\text{OC}_3\text{H}_7)_3$

Aluminum isopropoxide, $\text{Al}(\text{OPr}^i)_3$ dissolves well in benzene and toluene predried with molecular sieves. Toluene was used rather than benzene because of the carcinogenic hazard of the latter solvent.

A solution of 1.2M (20 wt %) of aluminum isopropoxide was sprayed at furnace temperatures varying from 250°C to 850°C. Above 400°C, a loose white powdery deposit was formed on the glass substrate surface. Less coating was formed on the substrate surface as the temperature was raised.

Coatings produced after the glass substrate had been held at a furnace temperature of 200°C for 12 minutes showed a fine non-adhesive white powder and a layer of adhesive white film. The coating could be scratched away, but could not be removed with a pressure sensitive tape.

A more extensive trial was conducted in which spraying was conducted at a furnace temperature between 200 and 400°C. The temperature was increased by 50°C for each run. The best coating was produced after the glass was held in the furnace at 300°C for 10 minutes. At furnace temperatures of 200 and 400°C, white non-adhesive powders were produced during these trials. Subsequent heat treatment at 850°C for 2 min. of a glass sample sprayed at 300°C gave a white non-adhesive powder.

Data are given in Appendix D, Table D7.

5.3.6.2 Al(C₄H₉O)₃

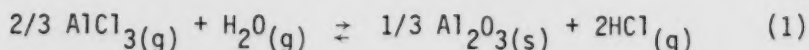
Several spraying runs were also carried out with aluminum sec-butoxide in propanol but due to the blocking of the passages mentioned above these trials were not pursued further. A differential scanning calorimetry (DSC) run was used to establish the decomposition temperature of aluminum sec-butoxide. The DSC run showed that decomposition occurred between 224.5 and 232.5°C.

5.3.7 Theoretical Studies of Al₂O₃ Coatings

5.3.7.1 Thermodynamic Studies of AlCl₃ Oxidation

The formation of a powdery deposit in many of the spray pyrolysis runs using a variety of aluminum compounds suggests that the reaction which yields Al₂O₃ is thermodynamically highly favourable. We will use the same approach outlined earlier for SnO₂ (Section 5.2.2.1) to demonstrate the conditions under which Al₂O₃ can be formed.

Starting with anhydrous AlCl₃ the reaction is



ΔG°_f and K values are presented in Table 4.

Table 4. ΔG_T° and K values for Reaction (1)

T(K)	ΔG_T° (Kcal)	K
300	-25.926	7.7×10^{18}
500	-25.690	1.7×10^{11}
700	-25.579	9.7×10^7
900	-25.571	1.6×10^6
1100	-25.651	1.2×10^5

Assuming the coefficient of the activity of Al_2O_3 is unity and partial pressure of AlCl_3 (P_{AlCl_3}) is close to 1 atm, the relationship of the partial pressures of H_2O ($P_{\text{H}_2\text{O}}$) and HCl (P_{HCl}) at various temperatures is shown in Figure 5.

It can be seen that the reaction strongly favours the formation of Al_2O_3 . To shift the reaction more toward the AlCl_3 side of the equation the following steps can be taken:

- (i) lower the P_{AlCl_3}
- (ii) lower the $P_{\text{H}_2\text{O}}$
- (iii) increase the P_{HCl}
- (iv) increase the temperature.

The equilibrium constant K for the reaction is

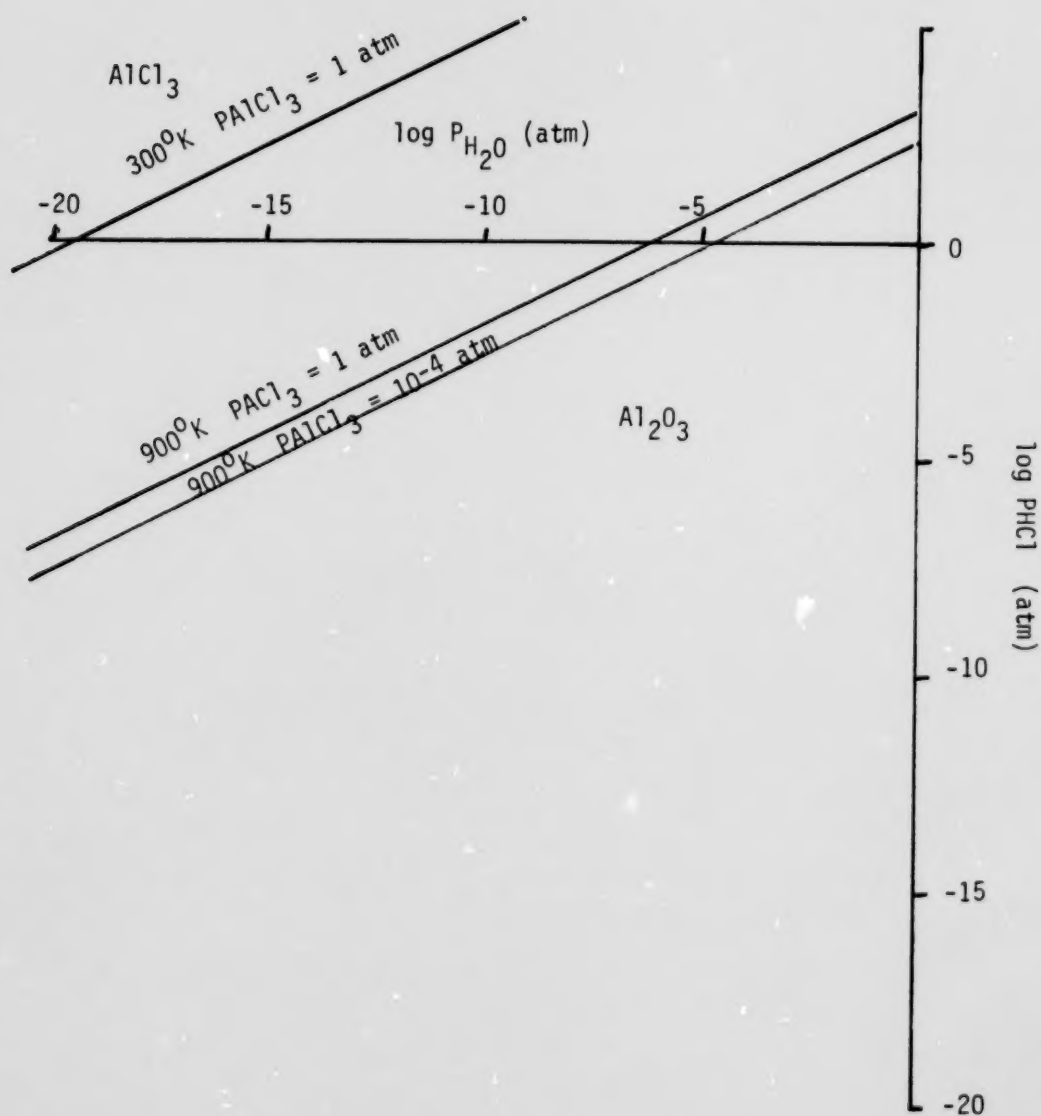
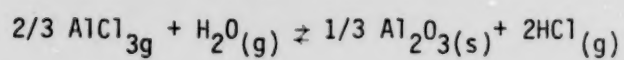
$$K = \frac{P_{\text{HCl}}^2}{P_{\text{AlCl}_3}^{2/3} \cdot P_{\text{H}_2\text{O}}} \quad (2)$$

Assuming that $P_{\text{AlCl}_3} = 1$ atm we obtain

$$K' = \frac{P_{\text{HCl}}^2}{P_{\text{H}_2\text{O}}} \quad (3)$$

Figure 5.

Relationship of P_{H_2O} and P_{HCl} for the Reaction



or

$$\log P_{\text{HCl}} = \frac{1}{2} \log K' + \frac{1}{2} \log P_{\text{H}_2\text{O}} \quad (4)$$

Typical humidity values are about 5 mm Hg of water vapor at room temperature. This implies $P_{\text{H}_2\text{O}} \sim 0.01$ atm. Using anhydrous AlCl_3 and an organic solvent the actual water vapour pressure could be further lowered through displacement of air by the evaporated solvent. A $P_{\text{H}_2\text{O}}$ value of 1×10^{-4} atm is probably the lowest possible water vapor pressure attainable. Rewriting equation (2) we get

$$\frac{P_{\text{HCl}}^2}{P_{\text{AlCl}_3}^{1/3}} = K \cdot P_{\text{H}_2\text{O}} \quad (5)$$

For the highest temperature in Table 5, 1100K, we find : $K = 1.2 \times 10^5$

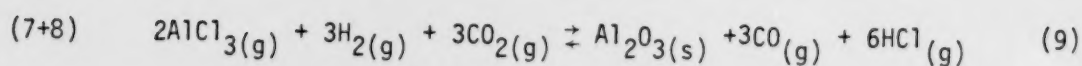
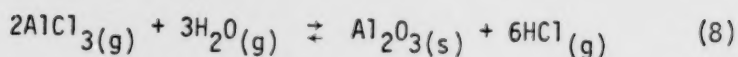
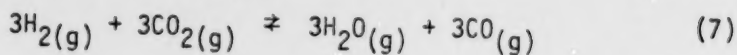
With $P_{\text{H}_2\text{O}} = 10^{-4}$ atm, equation (5) becomes

$$\frac{P_{\text{HCl}}^2}{P_{\text{AlCl}_3}^{2/3}} = 12 \quad (6)$$

The highest possible value for $P_{\text{HCl}} = 1$ atm, assuming the entire atmosphere in the spray booth is hydrogen chloride gas. This, then would give : $P_{\text{AlCl}_3} \sim 0.02$ atm. The assumption of a pure hydrogen chloride atmosphere is somewhat unrealistic. Lowering the P_{HCl} will substantially lower the P_{AlCl_3} and reduce the possible yield. For example for $P_{\text{HCl}} = 0.1$ atm, $P_{\text{AlCl}_3} \approx 2 \times 10^{-5}$ atm. The only viable options is to lower the $P_{\text{H}_2\text{O}}$ and increase the substrate temperature.

The reaction conditions are achieved in the CVD process used to produce alumina coatings utilizing cemented carbide substrates were the subject of a recent thermodynamic analysis by Colmet and coworkers (10).

The analysis was based on the reaction between $\text{AlCl}_3(\text{g})$, $\text{H}_2(\text{g})$ and $\text{CO}_2(\text{g})$ which proceeds according to the equations:



Reaction (7) lies well to the left since $K \sim 10^{-5}$ at 1300K. Thus, the use of a mixture of H_2 and CO_2 gases in the CVD set-up reduces the H_2O partial pressure to the point where the formation of Al_2O_3 is sufficiently slow to allow an equilibrium situation to occur. Typical experimental conditions in a CVD experiment are shown in Figure 6.

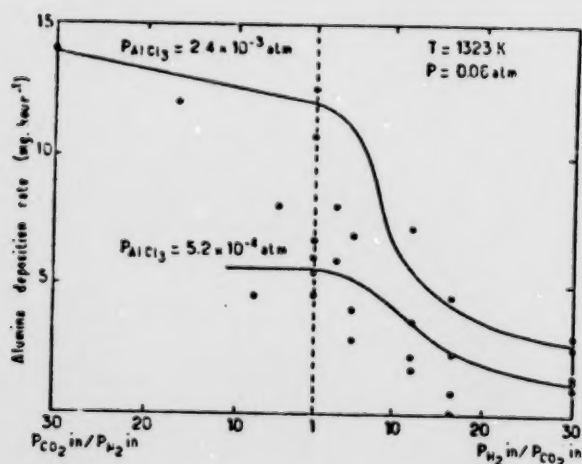


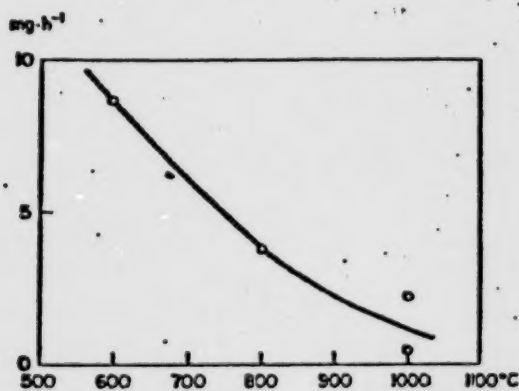
Figure 6. Experimental variation of the alumina deposition rate as a function of the partial pressure ratio of H_2 and CO_2 .

From ref. 10

It may be possible to approach the CVD reaction by flushing the spray booth with a gaseous mixture containing H_2 and CO_2 (e.g. a three component mixture: CO_2 , H_2 , Ar or CO_2 , H_2 , N_2).

5.3.7.2 Reaction Kinetics

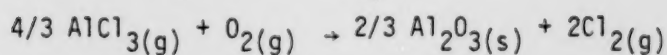
Funk and coworkers (11) reported that the rate of hydrolysis of AlCl_3 decreased as the reaction temperature increased. Figure 7 shows that decrease in deposition rate with temperature (11).



From ref. 11

Fig. 7 H_2O -process: Deposition rate as a function of substrate temperature (substrate:ISO P30; total pressure: 5 Torr; partial pressures: AlCl_3 -0.02, H_2O -0.05, H_2 -4.92 Torr; linear gas velocity at 200°C: $9.4 \text{ cm}\cdot\text{sec}^{-1}$).

The reaction between AlCl_3 and O_2



is imperceptibly slow (12) although the reaction is thermodynamically favorable (see Table 5 and Figure 8).

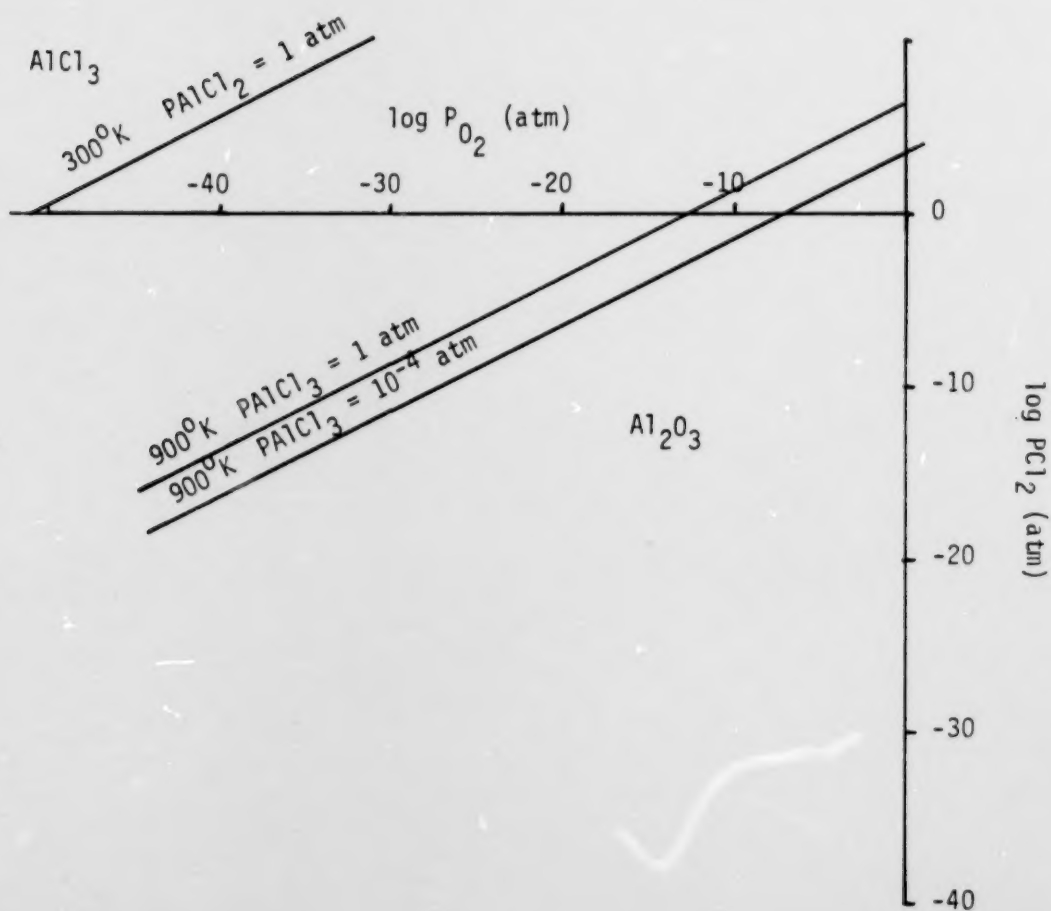
TABLE 5

 ΔG_T^0 and K values for the $O_2/AlCl_3$ system.

T(K)	ΔG_T^0 (Kcal)	K
300	-70.27	1.6×10^{51}
500	-63.53	5.9×10^{27}
700	-56.91	5.9×10^{17}
900	-50.44	1.8×10^{12}
1100	-44.11	5.8×10^8

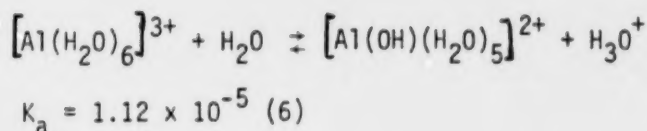
Figure 8.

Relationship of P_{O_2} and P_{Cl_2} for the Reaction
 $4/3 AlCl_3(g) + O_2(g) \rightleftharpoons 2/3 Al_2O_3(s) + 2Cl_2(g)$

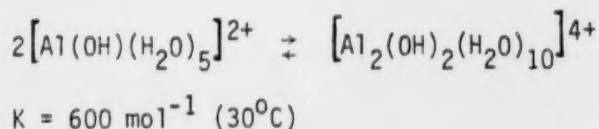


5.3.7.3 Reaction Mechanism

The Al^{3+} ion in water forms the hexaquaion, $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$. The common aluminum salts (chlorides, sulfates, nitrates, etc.) are partially hydrolyzed in water. This accounts for the acidity of their solutions.



Dimerization occurs readily



The presence of still more complex species of general formula $\text{Al}[\text{Al}_3(\text{OH})_8]_m^{m+3}$ has also been postulated ⁽⁶⁾. The conclusion is that aluminum salts in aqueous solution are already polymerized to a substantial extent. The high degree of polymerization contributes to the premature formation of Al_2O_3 powders before the substrate is reached.

5.3.7.4 Summary

It was found that solutions of simple aluminum compounds used in spray pyrolysis to-date give coatings which show a tendency to be powdery and which adhere weakly to the window glass substrate. The underlying reason is the rapid rate at which alumina is formed using oxygen from H_2O derived from the solvent or the atmosphere. Using AlCl_3 as a solute it is recommended that a suitable H_2 and CO_2 containing atmosphere be used to reduce the amount of water vapor.

With compounds containing Al-O bonds, the situation is somewhat the reverse. Since the tendency to form Al_2O_3 is reduced, compounds such as $\text{Al}(\text{NO}_3)_3$ when sprayed contain residual aluminum nitrate as is evident from the Raman spectra.

Another option further to be explored is the use of chelating agents. An example is acetylacetones which forms a volatile compound with aluminum. The compound boils at 315°C , and is easily soluble in ethanol, ether and benzene. Trials using these compounds have not been completed.

A thermodynamical approach was used to show the conditions (partial pressures of gases, temperatures) which favor the film formation.

5.4 Mixed $\text{SnO}_2/\text{Al}_2\text{O}_3$ Coatings on Window Glass Substrates

Adherent transparent abrasion resistant coatings of SnO_2 are produced when aqueous solutions of SnCl_4 are sprayed onto window glass substrates. Investigations have been carried out to establish to what extent alumina could be incorporated in SnO_2 coatings.

5.4.1 Solution Development

Since SnCl_4 in aqueous solution produces transparent adherent coatings on glass substrates, the initial trials aimed at producing mixed $\text{SnO}_2/\text{Al}_2\text{O}_3$ coatings on glass were carried out using AlCl_3 in conjunction with SnCl_4 . Both dilute and concentrated solutions were used.

5.4.1.1 Dilute Solutions

Mixed aqueous solutions were prepared from $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (0.22-0.45M) and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (0-0.34M) at a low total weight percentage (15% by weight) with $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}/\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ratios of 4/1, 3/2, 1/1, 2/3 and 1/4. pH Values ranged from 0.3 - 0.6. The furnace temperature and time were 850°C and 2-3 min., respectively. These conditions were those found to be the best furnace temperatures and times for SnO_2 coatings. It was observed that an increase in the aluminum chloride concentration reduced the adhesion of the coating. Also, the coatings with increased AlCl_3 content showed a more powdery appearance. For example, a mixed solution containing 0.22M $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and 0.34M $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ produced a coating with little adhesion and a heavy, white powdery deposit. On the other hand, a mixed solution containing 0.45M $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and 0.06M $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ produced a fairly adhesive coating with only a small amount of non-adhesive white powder

present. A solution containing no $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ produced a good transparent SnO_2 coating.

5.4.1.2 Concentrated Solutions

Coatings produced by a single spray burst of a dilute mixed solution were too thin for the microhardness test. A series of coatings were, therefore, produced using more concentrated solutions. The concentration ranges were 4.28-11.5M for $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and 0-1.04M for $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, respectively. The trends observed with the concentrated solutions paralleled those reported for the dilute solutions, i.e. the adhesion of the coating decreases while the deposit appears more powdery with increasing the $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ concentration. A 11.5M (80 % by wt.) $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ solution without $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ produced a transparent coating with excellent adhesion.

Data are given in Appendix D, Table D8.

5.4.2 Hardness Measurements

Microhardness measurements were performed on the coatings using a Leitz Miniload Microhardness Tester with a Knoop indenter and 100 g loads. For comparison, microhardness readings were taken in three places; the central region and the edge region of the coated side and the (uncoated) backside of the substrate. Hardness measurements were taken from coatings produced by $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}/\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ concentrated solutions. Coatings produced by diluted solutions were too thin for microhardness testing using a 100 g load. The coating produced by $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ without $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ had the highest hardness value. Increasing the concentration of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ in the solution reduced the hardness of the coating (with the possible exception of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}/\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ in a ratio of 4.28M/1.08M) as shown in Figure 7 and Table 6.

Coatings produced by reheating and respraying were harder than the single sprayed coatings (see Table 7). Reheating cycles of 10-60 seconds at 850°C were used. A 60 second cycle caused the glass to deform while a 30 second cycle yielded some deformation but increased its hardness value. The best hardness of the coatings produced equals to that of chromium

TABLE 6

Hardness Values of Samples

Sample #	Solution Composition (M) $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$	Hardness Value (KHN)		
		Centre (Coating)	Edge (Coating)	Back (no Coating)
69	11.5 0	876	882	558
71	6.66 0.46	735	770	547
73	4.28 1.04	838	749	550
77	8.56 0.22	807	791	530

TABLE 7

Hardness Values of Reheated Samples

Sample #	Repeated* Cycle	Solution Composition (M)		Hardness Value (KHN)		
		$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$	$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$	Centre (Coated)	Edge (Coated)	Back (no Coating)
98	10/5	6.66	0.46	889	756	547
99	-	6.66	0.46	868	773	530
100	-	4.28	1.04	728	644	506
101	10/5	4.28	1.04	773	755	518
103	2x 10/5	4.28	1.04	791	784	497
104	30/5	6.66	0.46	945	deformed	497
105	60/5	6.66	0.46	---	total deformation	----

* reheated cycle (second)/resprayed cycle (second)

and quartz (see the general hardness chart in Table 1).

5.4.3 Abrasion Resistance Testing

Preliminary abrasion resistance tests were carried out on coated and uncoated glass substrates to establish methodology. A method similar to the ASTM C-158-80 standard Section A2.4 entitled "Grit Blast Abrasion for Specimens of Rectangular Section" (Appendix F). Silicon carbide grit No. 120 (average 102 μm) and substrate with an exposed area of 3/8" diameter (shielded by an aluminum plate) were used for the test. It was found that using a 5g of SiC grit with an air pressure of 10 psi gave the best testing conditions, although the No. 120 grit SiC was too coarse for this abrasion test. The tested sample was examined under an optical microscope (320X). The depth of the eroded surface was measured in microns. A comparison of the measurements of the coated and uncoated glass as well as the mass loss of the sample will be used to monitor the abrasion resistance of the coatings. The abrasion resistance results of the coated SnO_2 , $\text{SnO}_2/\text{Al}_2\text{O}_3$ and Al_2O_3 and uncoated window glass substrates are listed in Table 8. Because of a better coating adhesion, SnO_2 coated window glass showed the best results on abrasion resistance.

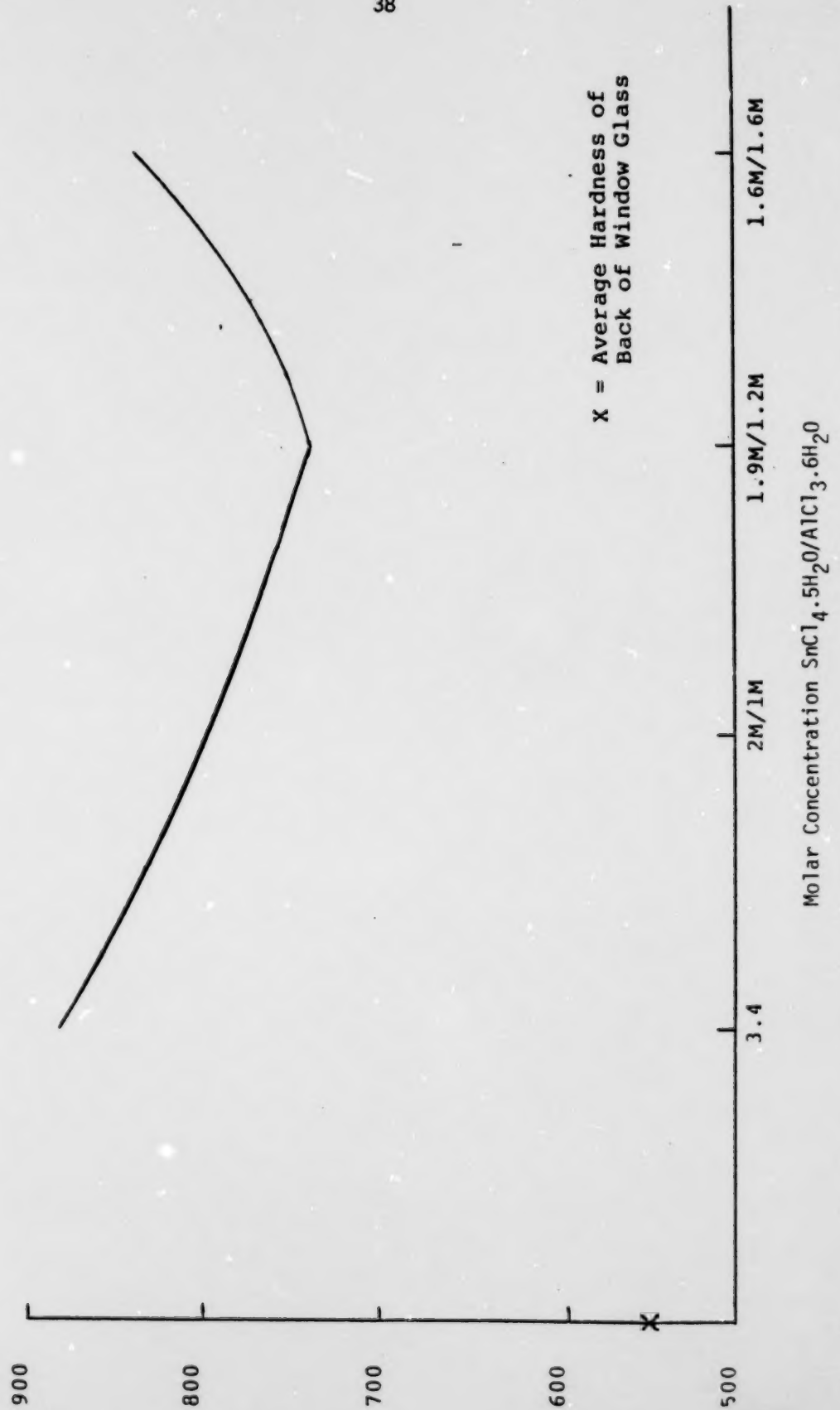
TABLE 8 *

Results on Abrasion Resistance

Coating on Glass	Source of Coating	Depth of Abrasion (microns)
None	-	4
SnO_2	$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ ($\text{H}_2\text{O}/\text{HCl}$)	< 1
$\text{SnO}_2/\text{Al}_2\text{O}_3$	$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}/\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ($\text{H}_2\text{O}/\text{HCl}$)	2
Al_2O_3	$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ($\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH}$)	4

* No mass loss measurements were carried out in these preliminary tests.

Figure 9
Hardness (Knoop Hardness Number) vs. Molar Concentration
 $\text{SnCl}_{4.5}\text{H}_2\text{O}/\text{AlCl}_{3.6}\text{H}_2\text{O}$



5.4.4 Mixed Coatings Using Al_2O_3 Powder

Deposits were also produced using aqueous $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ solutions in which there was a suspension of Alcan C71 (a fine reactive alumina powder). The adhesion of these coatings to the glass was poor. The alumina powder, heavily deposited on the glass surface gave the coating a poor appearance. The SnO_2 coating was not thick enough to bond the alumina particles to the glass surface.

Data are given in Appendix D, Table D9.

5.4.5 Layered $\text{SnO}_2/\text{Al}_2\text{O}_3$ Coatings

SnCl_4 solutions in H_2O produce adherent transparent coatings by spray pyrolysis. This property of aqueous SnCl_4 solutions was used to produce coatings incorporating Al_2O_3 . For this purpose, sequential spray cycles with $\text{SnCl}_4/\text{AlCl}_3$ solutions were carried out. The initial spray cycle used a 50 wt.% $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ solution. Subsequent spray cycles used 45/5 wt.% $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}/\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, 40/10 wt.% $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}/\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, 25/25 wt.% $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}/\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$. Furnace temperatures ranged from 600-850°C.

This method did not produce adhesive Al_2O_3 containing coatings. A transparent SnO_2 was formed with a loose flaky white powdery layer on top. The amount of powder formed was found to increase with the weight % of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ in solution.

Glass substrates that were sprayed by an aqueous solution of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were reheated and resprayed by an aqueous solution of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$. Although the adhesion of the coating improves, some of the coating can still be removed by the pressure sensitive tape.

Data are given in Appendix D, Table D10.

5.5 ZrO₂ Coatings on Window Glass Substrates

5.5.1 Initial Trials

N-Butyl Zirconate was used for the deposition of ZrO₂ coatings on glass substrates. Transparent and adhesive ZrO₂ coatings have been produced.

At a furnace temperature of 300°C, the deposit was a white non-adhesive powder. Further heat treatment of the coating in the same furnace, the deposit turned yellowish and the adhesion of the deposit to glass improved. At a furnace temperature range of 450-750°C, an adhesive and transparent coating was produced. Second or further depositions adhered firmly to the previous coating. The overall coating remained transparent. The coatings show a pattern of Newton's rings.

Data are given in Appendix D, Table D11.

5.5.2 Single Sprayed Coatings

To establish the effect of temperature, a series of ten second single sprayed coatings with no further heat treatment were carried out at furnace temperatures of 400°C - 800°C. At a furnace temperature above 450°C, transparent and adhesive coatings were produced (Figure 10). The circular patterns of the coatings were reduced at higher temperatures (Figure 11) (above 550°C). Generally, no cracks were found on the single coatings (thin deposits) sprayed at the higher temperatures (above 550°C). In several spots hairline cracks were found originated from the inclusions (heavier deposits) (Figure 12).

Data for this series are given in Appendix D, Table D12.

X-ray powder diffractrometry was carried out on the sprayed glass samples. Besides a strong amorphous component from the glass substrate there were two peaks which can be attributed to either cubic

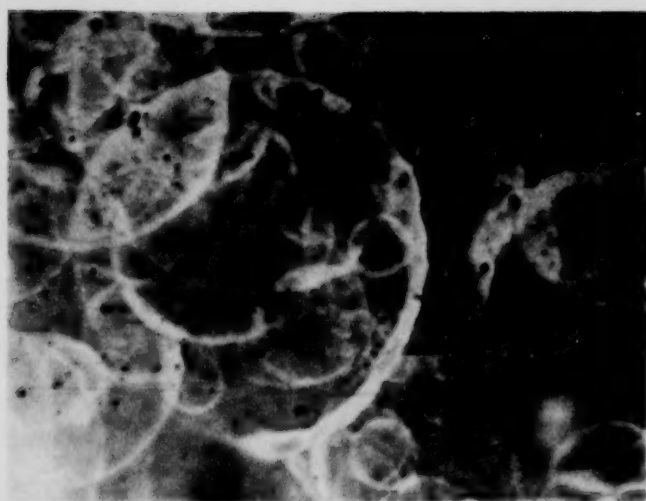


Figure 10.

Optical Micrograph

ZrO₂ Coatings on Sample #357
(450°C - single coats)

X370



Figure 11.

ZrO₂ Coatings on Sample #361
(600°C - single coat)

X370



Figure 12.

ZrO₂ Coatings on Sample #365
(650°C - single coat)

Fine Cracks

X370

or tetragonal ZrO_2 . These two ZrO_2 polymorphs are not easily distinguished since they give similar X-ray patterns (see Table 9).

Knoop microhardness tests were performed on the ZrO_2 coated glass substrates. A load of 10g applied. The small size of indentations did not give consistent Knoop hardness values (see Table 10).

Abrasion resistance tests were carried out with a sandgrit blaster using 5g of #120 grit SiC with 20 psi for 30 sec. to a 3/8" dia. exposed area. Again, the sandblast conditions were too severe for the thin film. Results based on the weight loss did not show any differentiation between the coated and the uncoated glass samples (see Table 11).

5.5.3 Multi-Sprayed Coatings

- (a) A series of multi-sprayed (5 sprays + 5 heat treatments) coatings were carried out at various furnace temperatures (400-800°C). It was found that cracks in the transparent coatings were formed at a furnace temperature above 600°C.

These cracks were believed to be the shrinkage cracks caused by the phase changes of the ZrO_2 coating. Mazdiasni⁽¹³⁾ described the metastable transitions of zirconia obtained from decomposition of alkoxides at 300°C and 400°C. At a furnace temperature of 550°C, zirconia coating produced were free of cracks and contained very few circular patterns.

Results are listed in Appendix D, Table D13.

TABLE 9. X-Ray Diffraction Patterns of ZrO_2 Coatings (single coat).

cubic ZrO_2 d °A	tetragonal ZrO_2 d °A	Coatings above 650°C d °A
2.92	2.95	2.94
2.53	2.54	2.58
1.81	1.80	
1.53	1.54	

TABLE 10. Hardness Values of Single Sprayed ZrO_2 Coatings.

Sample No.	Sprayed Temperature °C	Knoop Hardness No.	KHN (average)
Plain glass	-	112 - 127*	-
356	400	145 - 175	160
357	450	264 - 394	330
358	500	317 - 817	530
359	550	600 - 829	757
361	600	632 - 650	640
362,365,367	650	624 - 869	760
369	700	804 - 869	836
364	750	829 - 842	835

* Soda-lime glass should have KHN ~ 450-550.

TABLE 11. Abrasion Resistance of Single Spray ZrO_2 Coatings (Sandblast, #120 SiC 5gm, 20 psi, 30 second).

Specimen No.	Sprayed Temperature °C	Wt loss mg	Average wt loss mg
374(Plain Glass)	550	.22 - 1.09	0.77
357	450	.56 - 4.29	2.43
358	500	.53 - 1.56	1.05
359	550	.45 - .63	0.54
361	600	.92 - .94	0.93
362	650	.98 - 1.19	1.10
369	700	1.04 - 1.30	1.17
364	750	1.3 - 1.34	1.32

- (b) To gain more insight in the conditions that lead to the formation of crystallinity an experiment was carried out where the coating was built up from a single to a double layer at a furnace temperature of 550°C.

The x-ray powder diffractrometry on the coatings generally showed no peaks besides a strong amorphous component from the glass. For one coating, a small peak which can be attributed to either cubic or tetragonal ZrO_2 can be seen on the x-ray powder diffraction patterns. Generally, the coatings are believed to be amorphous ZrO_2 .

Abrasion resistance tests were carried out with a sand grit blaster. Again, results based on the weight loss did not show any significant differentiation between the coated and the uncoated glass samples (see Table 12).

Data can be found in Appendix D, Table D14.

- (c) A series of coatings from single to 20 sprays and with or without heat treatment were carried out at a furnace temperature of 700°C.

With 20 sprays, heavy, white and translucent ZrO_2 coatings were produced.

Under 10 sprays, coatings remained transparent. (See Figure 13)

Optical micrographs of these coatings are shown in Figure 14, 15 and 16. For coatings thickness measurement see Section 5.5.5.

X-ray powder diffractrometry showed 4 strong peaks which can be attributed to either cubic or tetragonal ZrO_2 . These peaks increased in intensity when more coatings were applied (see Table 13 and Figure 17).

Data can be found in Appendix D, Table D15.

TABLE 12. Abrasion Resistance of ZrO_2 Coatings
(Furnace Temperature : $550^{\circ}C$)

Specimen No.	Spray cycle	Wt loss mg	Average wt. loss mg
375(Plain glass)	-	.98 - 1.11	1.05
376(Plain glass)	-	1.13 - 1.17	1.15
377(Plain glass)	-	1.01 - 1.86	1.43
378	S	.91 - .96	.94
379	S	1.03 - 1.18	1.07
380	S	1.15 - 1.19	1.17
381	S	.28 - .87	0.58
382	S-HT	.78 - 1.03	0.91
383	S-HT	.52 - 1.50	1.01
384	S-HT-S	.45 - .58	.52
385	S-HT-S	.89 - 2.21	1.55

S - 10 second sprayed

HT - 4 minute heat treatment in the furnace

TABLE 13. X-Ray Diffraction Patterns of ZrO_2 Coatings
(Furnace Temperature $700^{\circ}C$)
Specimen No. (438, 441, 443)

Cubic ZrO_2 $d^{\circ}A$	tetragonal ZrO_2 $d^{\circ}A$	Coatings ($700^{\circ}C$) $d^{\circ}A$
2.92	2.95	2.95
2.53	2.54	2.55
1.81	1.80	1.80
1.53	1.54	1.53

Figure 13.

 ZrO_2 Coating Appearance

(from left to right: 5 coats, 10 coats
and 20 coats at 700°C).



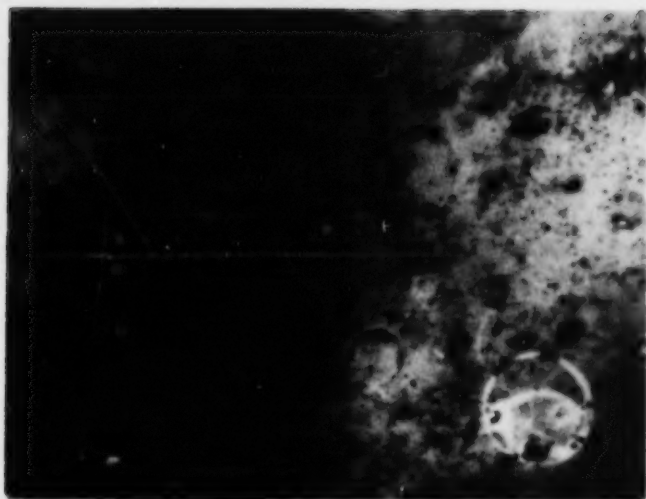


Figure 14

Optical Micrograph ZrO_2
Coatings on Sample #438
(700°C - 5 coats)

X370

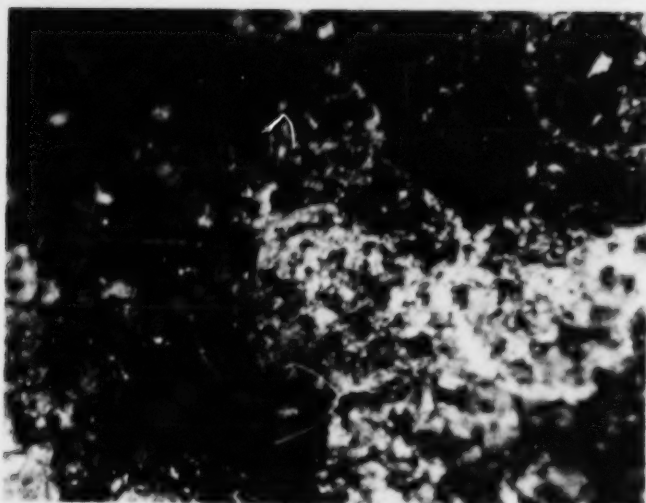


Figure 15

ZrO_2 Coatings on Sample
#441
(700°C - 10 coats)

X370

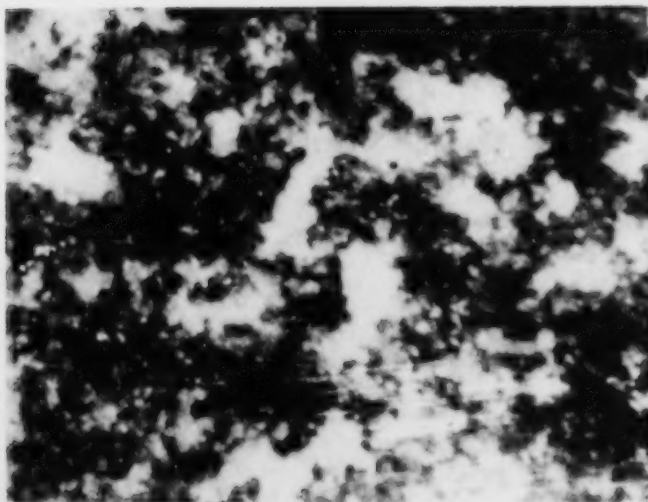


Figure 16

ZrO_2 Coatings on Sample
#442.
(700°C - 20 coats)

X370



5.5.4 Electron Optical Studies

Selected ZrO_2 coated specimens (No.383 and 432) were examined under the optical microscope and under the scanning electron microscope (SEM) (Figures 18 and 19). The spraying conditions for the two specimen are:

Specimen No.	Furnace Temperature $^{\circ}C$	Number of Coats
383	550	5
432	700	3

Electron Micrographs and EDXA spectra can be found in Appendix H.

(a) Specimen No. 383 (Figure 18)

ZrO_2 coatings had a nodular structure. The nodules were approximately 0.2-0.4 μm in diameter (Figure H1a and b). The composition of the coatings was analyzed by E.D. X-Ray Spectra. The high peaks of Zr in the background of Si, Ca, Mg, Na (Soda lime -glass) indicated that the coating is ZrO_2 . (Because of high x-ray penetration ($\sim 2-3\mu$), the E.D. X-Ray Spectra will include the substrate (soda-lime glass) spectra). A hafmium impurity from the ZrO_2 coating is also observed.

The circular pattern seen on several ZrO_2 coatings were also examined under the SEM (Figure H3 a and b). The morphology of the region was similar to that of other areas of the coatings.

From the fracture surfaces of ZrO_2 coated glass, the thickness of the ZrO_2 coatings was estimated to be 0.5 μm (Figure H4). Again E.D. X-Ray Spectra of the soda-lime glass and the ZrO_2 coatings were produced (Figure H5, H6). The difference between the two regions is clearly observed. The presence of soda-lime glass in the ZrO_2 coating spectra was due to the scattering effect.

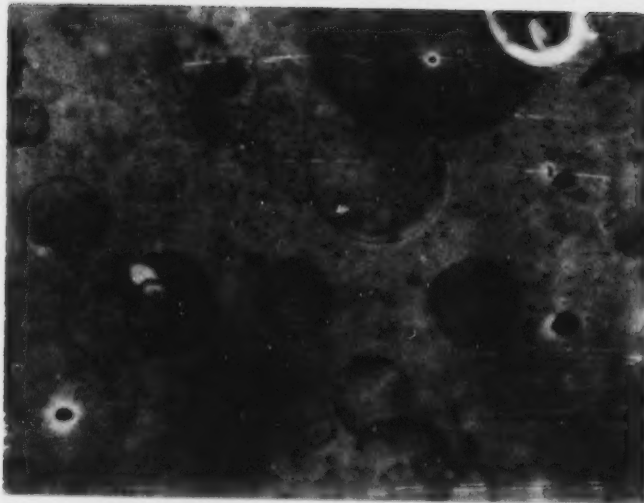


Figure 18

Optical Micrograph

 ZrO_2 Coatings on Samp #383
(550°C - 5 coats)

X370

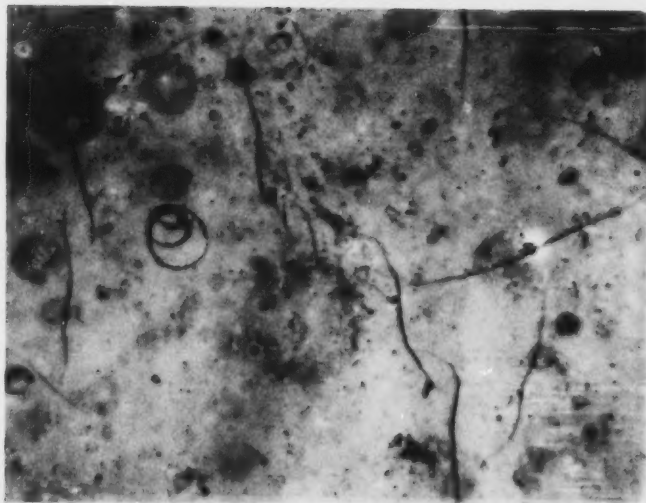


Figure 19

 ZrO_2 Coatings on Sample
#432

(700°C - 3 coats)

X370

(b) Specimen No. 432 (Figure 19)

ZrO₂ coatings had a nodular size of 0.1-0.2 μm (Figure H7, a and b). The hairline crack of the coatings is revealed in Figure H8. The E.D. X-Ray Spectra of the specimen (Figure H9 a and b) show relatively smaller peaks for Zr than was observed for specimen No. 383. This indicated a thinner zirconia coating on the specimen (3 coats vs 5 coats, 700°C vs 550°C).

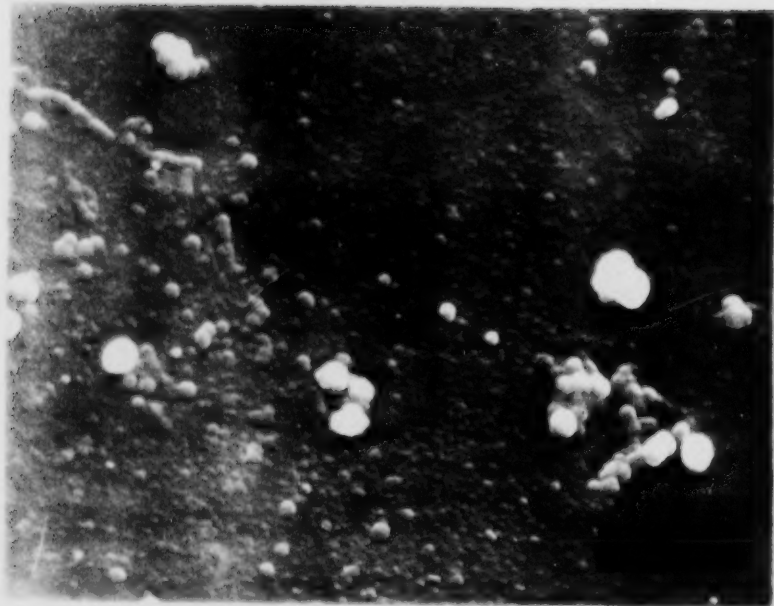
5.5.5 Coating Thickness

A series of fractured edge of ZrO₂ coated glass specimens (No. 439, 441 and 443) were examined under SEM (Figures 20, 21 and 22). These specimens were produced at a furnace temperature of 700°C with 5, 10 and 20 sprays respectively. Using electron micrographs, the thickness of these ZrO₂ coatings were estimated as follows:

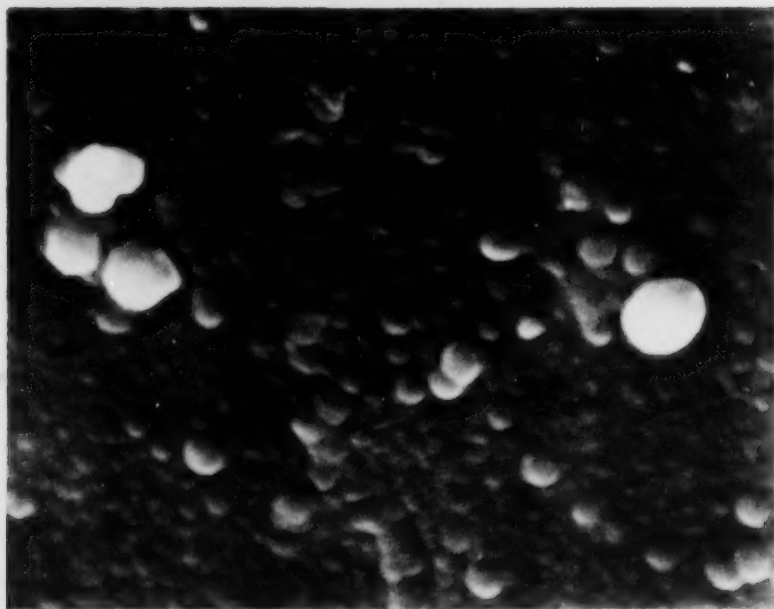
Specimen No.	Furnace Temperature	No. of Coats	Appearance	Coating Thickness μm
439	700°C	5	Transparent	0.2
441	700°C	10	Transparent	0.4
443	700°C	20	White, translucent	0.8

5.5.6 Theoretical Considerations

Mazdiyasni and coworkers ⁽¹⁴⁾ have proposed a mechanism for the decomposition of zirconium tetratertiary butoxide (see Figure 23). The decomposition proceeds



(a)



(b)

Fig. 20 SEM micrographs of ZrO₂ coating surface on Window Glass

Figure 21.

Fractured Edge of ZrO_2 Coated Glass under SEM. (Sample #440, 700°C , 10 coats)

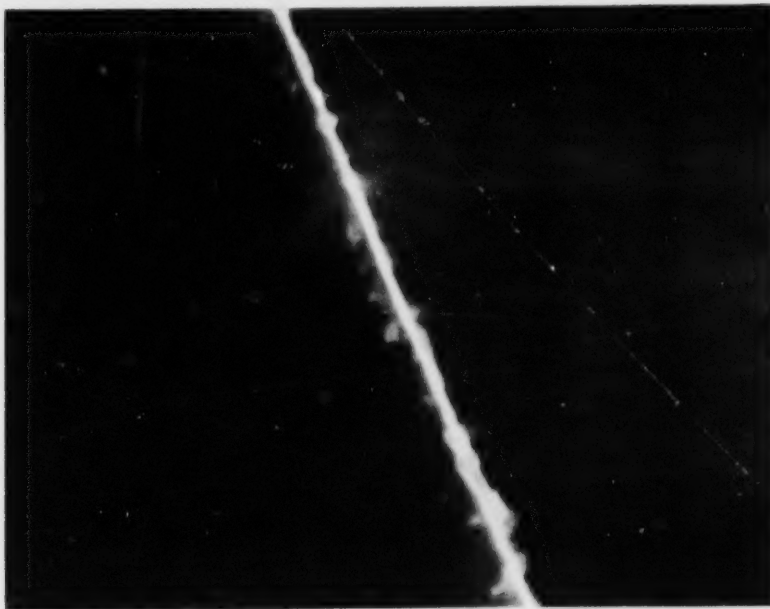
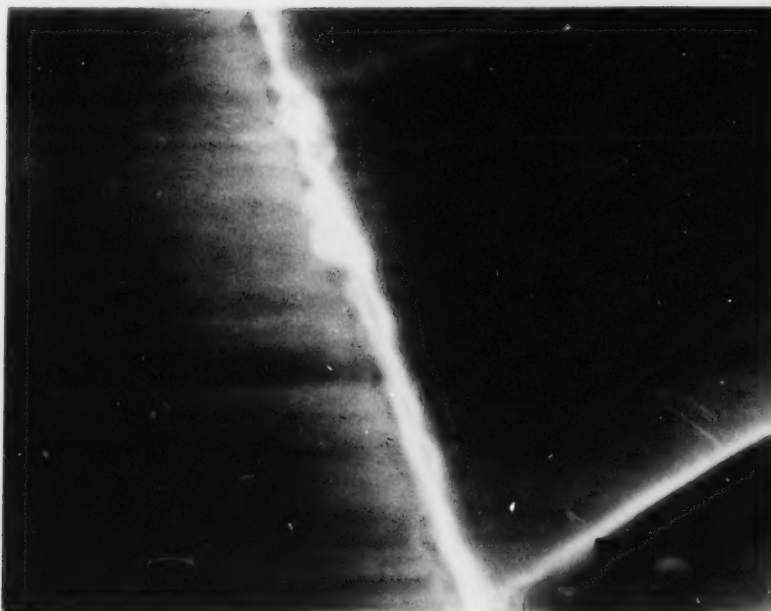


Figure 22

Fractured Edge of ZrO_2 Coated Glass under SEM. (Sample #443, 700°C , 20 coats)



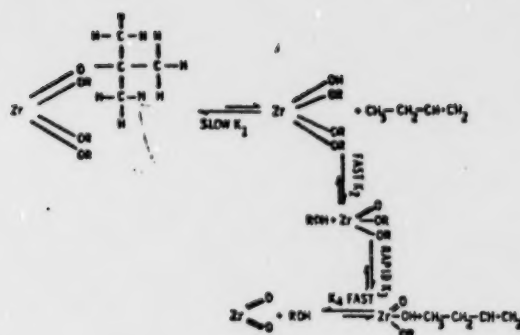
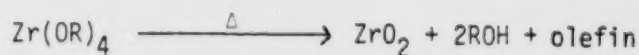
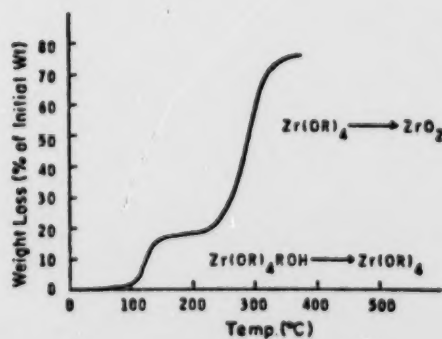


Figure 23. The decomposition of Zr(OR)_4 to ZrO_2 according to the overall reaction



The first hydrolysis step is slow but all subsequent steps are fast. Figure 15 shows a weight loss temperature profile for the reaction



From Ref. 14

Figure 15. Decomposition of zirconium alkoxides in N_2 atmosphere.

Mazdiasni found that cubic ZrO_2 powders were formed during heat treatment up to 300°C and that the transformation to cubic zirconia was virtually complete at 700°C . In the spray pyrolysis trials carried out under this program we believed that we found amorphous zirconia at furnace temperatures up to 550°C and cubic/tetragonal zirconia at higher furnace temperatures.

5.5.7 TiO_2 Coatings on Window Glass

Isobutyl titanate was used for the deposition of TiO_2 coatings on glass substrates. At a furnace temperature of 500°C , adhesive and semi-transparent TiO_2 coatings were produced. Further deposition adhered firmly to the previous coating. The microhardness value of the coatings were ≈ 620 KHN at the centre and ≈ 680 KHN at the edges. Glass hardness values of ~ 500 KHN were observed on the back side of the specimen.

Data are given in Appendix D, Table D16. No further work has been carried out in this system so far.

6. CONCLUSIONS AND RECOMMENDATIONS

On the basis of the results obtained to-date the following conclusions have been reached.

1. Adhesive transparent and translucent crystalline zirconia films of thicknesses up to $0.8\ \mu\text{m}$ have been deposited on glass substrates using the spray pyrolysis facility at ORF.
2. The deposition of zirconia and titania coatings from metal alkoxides show that these film precursors are potentially a useful class of compounds for spray pyrolysis.

3. Inorganic film precursor compounds will produce adhesive transparent tin (IV) oxide coatings. However, alumina coatings deposited from solutions of inorganic compounds appear powdery and adhesion is poor.
4. A thermodynamic analysis has indicated that the partial pressure of water vapor is the main obstacle which prevents the deposition of hard adhesive films of alumina from anhydrous aluminum chloride. Reducing the water vapor pressure is, therefore, a prerequisite to produce alumina coating from this source.

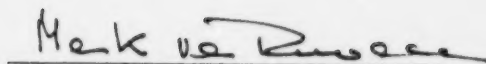
On the basis of these results it is recommended that work during Phase II be concentrated in the following areas.

1. Now the feasibility of depositing zirconia coatings by spray pyrolysis has been demonstrated further research and development work should be carried out to produce these coatings on metallic and ceramic substrates as well. Coating thickness should be increased and extensive testing should be carried out to measure hardness and abrasion resistance. In particular, the properties of coated substrates should be monitored during thermal cycling to establish whether these coatings have potential for thermal cycling applications. The incorporation of calcia or yttria for stabilization should be attempted.
2. The potential of metal alkoxides for the deposition of metal oxide films needs further attention. The use of this method for the deposition of alumina coatings should be further explored. A comparative thermodynamic analysis for zirconia and alumina may be helpful here.

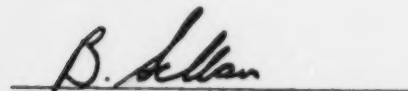
3. The option of reducing the water vapor pressure in the atmosphere during spraying with anhydrous solvents should be addressed. In particular, the use of a three component gas mixture, containing minor quantities of hydrogen and carbon monoxide deserves attention.



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APPENDIX A

Literature Survey

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1. INTRODUCTION

Spray pyrolysis is a technique for depositing a surface layer (usually an oxide) onto a substrate of a different material. The concept of applying an abrasion resistant coating onto a softer substrate is often referred to as "hard facing". It is investigated here to develop the technique of spray pyrolysis in order to deposit abrasion resistant oxide coatings on softer substrate materials.

Spray pyrolysis is not anticipated to duplicate other hardfacing techniques but would supplement them in several important areas. For example, aircraft parts can be hardfaced by plasma spray deposition of oxide coatings. Spray pyrolysis deposited oxide coatings would likely be similar in nature. However, the plasma spray process requires high capital investment (>\$100,000.) whereas the investment required for spray pyrolysis would be much lower. The plasma spray technique would likely have lower operating costs than the spray pyrolysis technique. Therefore, plasma spray oxide hardfacing would be more suited for large scale production and spray pyrolysis would be more suited to smaller scale production.

Spray pyrolysis is a special case of chemical vapour deposition (CVD). A solution containing the required reactants is simply sprayed onto a hot substrate. In CVD, a carrier gas stream transports the gaseous reactants onto a heated substrate. The advantage of spray pyrolysis over CVD is in the higher deposition rates achieved as well as a much lower equipment cost. The disadvantage of spray pyrolysis is that only a very limited set of reactants will produce an adherent, hard coating on the substrate.

Spray pyrolysis has been used extensively for the deposition of tin oxide onto glass substrates. Products ranging from glass containers to oven windows to liquid crystal displays use the tin oxide spray pyrolysis technique. Coatings of indium oxide, cadmium stannate, cadmium sulphide, copper-indium sulphide and other semiconducting compounds have been prepared by the spray pyrolysis technique. It is the object of this literature survey to investigate the scope of the spray pyrolysis technique and its potential for the deposition of abrasion resistant materials. To this end there is a general discussion of abrasion resistant coatings with specific reference to tin oxide, alumina and zirconia coatings, a chapter on spray pyrolysis, and chapters outlining the chemistries of tin, aluminum and zirconium compounds.

2. ABRASION RESISTANT COATINGS

2.1 Abrasion Resistant Materials

The reduction of abrasion damage to surfaces has received a great deal of attention over the years yet is not fully understood. Many methods of reducing abrasion damage have been developed depending on the situation. In the case of impingement of particles, very soft materials, such as rubber, have been used to reduce abrasion wear in pipelines and grinding mills when the abrading particles are small, soft and/or circular in shape. Rubber or other elastomer materials absorb the momentum of the impinging particle by elastic compression which is transferred back to the particle or other medium by the springback of the elastomer.

If the impinging particles are coarse, hard or have sharp edges then a hard material must be used such that the momentum of the impinging particle is used to fracture or deform the impinging particle rather than the target surface.

In many situations the abrasion wear on a surface is due to sliding wear of another surface or particle moving nearly parallel to the target surface. In this situation it is the scratch hardness which will be the primary factor in abrasion wear in a given situation⁽¹⁾. Particle size impact strength, hardness, shape and velocity will obviously affect wear rates in the case of particle sliding (e.g. pneumatic/hydraulic conveyors, shutes, hoppers, or slurry pipelines etc.). Sliding abrasion wear of surfaces is a complex function of applied force, existence of absorbed surface films, surface finish and coefficient of friction as well as the material properties of each surface such as hardness, scratch hardness, microstructure and composition^(1,3).

The combined action of corrosion and abrasion contributes to erosion of the target surface as well as the mode of operation. For example, intermittent operation can result in twice as much wear in unprotected hydraulic lines as is observed in continuous operation⁽¹⁾.

There are many mechanisms to abrasion wear. For impingement of particles the following mechanisms have been listed⁽¹⁾:

- plastic deformation/pitting/plowing
- grain pullout
- rounding of grains
- multi-grain chipping
- macroscopic crazing and chipping
- preferential wear of grain boundaries

In situations involving the sliding wear of two solid surface, the mechanisms of abrasion wear are slightly different. Some of these mechanisms have been listed as being ⁽³⁾:

- Adhesion wear:
(Plastic deformation of asperities to support the load. Shear of asperities can result in cleavage planes on both surfaces with subsequent ionic bonding. In order for adhesion wear to occur, the fracture strength of one (or both) material(s) must be less than the interfacial junction. Chemical bonding is important in some metal-ceramic interfaces as the chemical bond at contact points is often stronger than the shear strength of the metal or the ceramic grain. In this case softer material is often transferred to the surface of the stronger material.)
- Abrasive wear:
(Free particles of a harder material are generated and imposed at the interface between the two surfaces. These particles can cut into and remove material from softer surfaces).
- Friction:
(Shear of interlocking asperities is a function of surface finish, contact area, and surface films. The increase in the ability of some ceramic surfaces to deform plastically in the presence of surface active species is called the Rebinder effect).

- Plowing:

(The greater the deformability of one of two surfaces in contact, the deeper the second material can embed into the surface and is very important with ceramic-metal surfaces).

D.H. Buckley⁽³⁾ summarizes the differences between ceramics and metals as follows:

"Ceramics like metals behave in accordance with the adhesion theory of friction. Interfacial adhesion is a large component of measured friction forces. Ceramics usually exhibit lower friction coefficients than metals. The excellent resistance to wear characteristic of many ceramics can be attributed to the presence of surface films which minimize the formation of strong adhesive junctions and to their high elastic moduli minimizing the real contact area⁽³⁾".

"The presence of films on the surface of ionic solids effect the mechanical behavior of these materials during sliding. Surface-active agents increase the deformability of the surface during sliding thereby arresting crack formation.

"When metals contact ceramics, the ability of the metal to interact chemically with the ceramic surface plays an important role in observed friction and wear behavior. Friction forces and wear will be dictated by the zone of weakest bonding in the interfacial layers. It may occur in the ceramic, in the metal or at the interface⁽³⁾".

2.1.1 Ceramics

As mentioned in the preceding section, many ceramics exhibit excellent resistance to abrasion by particle impaction and sliding wear. The ceramics which have received the greatest attention are those which exhibit high strength and high hardness such as high alumina ceramics and glass-ceramics, zirconia and non-oxide ceramics such as silicon carbide and

silicon nitride. Other related materials include a wide variety of borides, carbides, nitrides, silicides and phosphides. The methods of applying these "hard" materials to substrates are discussed in a later section.

2.1.2 Metals

Metals can be chosen, coated or treated for higher abrasion resistance. In general, the higher hardness metals have better abrasion resistance. The higher hardness is usually imparted by alloy additions or by heat treatment. Electroplated metal coatings of harder metals (e.g. Cr or Ni on steel) can also be used to increase the abrasion resistance of metal surfaces.

Reaction of the metal surface layer to form the carbide, nitride, or boride of the base metal is an extremely commonly used technique for increasing the surface hardness of especially ferrous alloys. The formation of oxide films such as the case with anodizing is used with selected alloys.

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2.2 Coating Techniques (1)

Advanced engineering applications often demand materials which can perform under aggressive environmental conditions without suffering from a loss of bulk strength and specific surface properties. As the material performance requirements become more stringent, it becomes more impractical for a single material to satisfy all the diverse technical and economic requirements. Coating technology offers an attractive option of choosing a base material for purely economic reasons.

Protective coatings which can resist abrasion or corrosive and erosive environments are particularly useful. Various coating technology is reviewed in this section.

In general, deposition processes may be divided into two types:

- (1) those involving droplet transfer such as plasma spraying, arc spraying, wire-explosion spraying, detonation gun coating, and
- (2) those involving an atom-by-atom transfer mode such as the physical vapor processes of evaporation, ion plating, and sputtering, chemical vapor deposition, and electrodeposition.

The chief disadvantage of the droplet transfer process is the porosity in the final deposit which effects the properties.

There are three steps in the formation of any deposit:

- i. Synthesis of the material to be deposited
 - (a) Transition from a condensed phase (solid or liquid) to the vapor phase,
 - (b) For deposition of compounds, a reaction between the components of the compound some of which may be introduced into the chamber as a gas or vapor.

- ii. Transport of the vapors between the source and substrate.
- iii. Condensation of vapors (and gases) followed by film nucleation and growth.

2.2.1 Chemical Vapor Deposition (CVD) (1,2,3)

The CVD process utilizes gaseous phase chemical reactions to deposit solid materials on hot substrate surfaces. A wide range of metallic and ceramic coatings, including those refractory metals which for reasons of either chemistry, brittleness or high melting point, cannot be readily deposited by other methods, can be deposited by CVD. It enables thin dense coatings to be applied to components with complex-shaped internal surfaces.

Refractory coatings which are known for their superior performance under such conditions compared with most metals, require special coating techniques because of their higher melting temperatures. Chemical vapour deposition (CVD) provides a technique for obtaining coatings of refractory materials.

Reaction temperatures of CVD can be between about 200°C and 2200°C, but are mostly between 500-1100°C. The actual optimum temperature for a given reaction often lies within a very narrow range so that the whole process needs to be tailored to the substrate and to the intended application. The substrate melting point and its susceptibility to chemical attack by the reacting gases or by their side-products needs to be considered.

The separation between CVD and other forms of chemical vapour deposition such as plasma-activated CVD, chemical spray deposition and activated reactive evaporation, to name a few, lies in the method of activation of the chemical reactants. Conventional CVD is a process whereby suitable gaseous reactants are brought together in a reaction chamber and thermally activated under controlled conditions to produce a solid substrate deposit.

A simple CVD unit is shown in Figure 1.

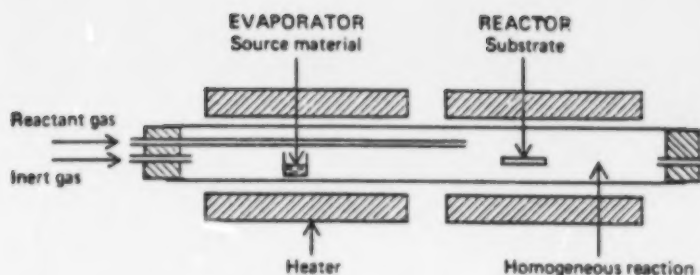


Fig. 1. Schematic representation of CVD reactor.

Ref. 1

CVD has most to offer under the following circumstances:

- (1) When the material to be deposited is refractory in nature (e.g. high melting point carbide or nitride).
- (2) When the surface to be coated is geometrically complex (e.g. inside of a control valve).
- (3) When the nature of the substrate imposes no limitation on the process temperature.
- (4) When a particular structure is required in the deposit (e.g. pyrolytic graphite).
- (5) When large numbers of small components are to be coated.

2.2.2 Physical Vapor Deposition (PVD) (1)

Physical vapor deposition (PVD) processes are originally applied to the deposition of single materials such as metals not involving chemical reactions. The versatility of the PVD processes led to the development of PVD processes for the deposition of compounds which necessarily involve chemical reactions. Thus, the distinction between CVD and PVD processes becomes less sharp.

A unique attribute of PVD processes is that the coating is not the result of a process such as solidification where the laws of physical

chemistry govern. They are "non-equilibrium" processes such that any coating may be deposited onto virtually any substrate.

Physical vapor deposition (PVD) technology consists of the techniques of evaporation, ion plating, and sputtering. It is used to deposit films and coatings or selfsupported shapes such as sheet, foil, tubing, etc. The thickness of the deposits can vary over a wide variety of applications from decorative to utilitarian over significant segments of the engineering, chemical, nuclear, microelectronics, and related industries.

PVD technology is very versatile, enabling one to deposit virtually every type of inorganic materials, metals, alloys, compounds and mixtures thereof, as well as some inorganic materials. The deposition rates can be varied from 10 to 250,000 Å (10^{-3} to 25 μm) per minute, the higher rates having come about in the last 20 years with the advent of electron beam heated sources.

Advantages and Limitations of PVD

There are several advantages of PVD processes over competitive processes such as electrodeposition, CVD, plasma spraying. They are:

1. Extreme versatility in composition of deposit. Virtually any metal, alloy, refractory, or intermetallic compound, some polymeric type materials and their mixtures can easily be deposited. In this regard, they are superior to any other deposition process.
2. The substrate temperature can be varied within very wide limits from subzero to high temperatures.
3. Ability to produce coatings or self-supported shapes at high deposition rates.
4. Deposits have very high purity.

5. Excellent bonding to the substrate.
6. Excellent surface finish which can be equal to that of the substrate.
7. Elimination of pollutants and effluants from the process which is a very important ecological factor.

The present limitations of PVD processes are:

1. Inability to deposit polymeric materials with certain exceptions.
2. Higher degree of sophistication of the processing equipment and hence a higher initial cost.
3. Relatively new technology and the "mystique" associated with vacuum processes, much of which is disappearing with education and familiarity.

2.2.3 Evaporation (1)

In the evaporation process, vapors are produced from a material located in a source which is heated by radiation, eddy currents, electron beam bombardment, a laser beam or an electrical discharge. The process is usually carried out in vacuum (typically 10^{-5} to 10^{-6} torr) so that the evaporated atoms undergo an essentially collisionless line-of-sight transport prior to condensation on the substrate. The substrate is usually at ground potential (i.e. not biased).

Figure 2 is a schematic of a vacuum evaporation system illustrating electron beam heating. It may be noticed that the deposit thickness is greatest directly above the center-line of the source and decreases away from it. This problem is overcome by imparting a complex motion to substrates (e.g. in a planetary or rotating substrate holder) so as to even out the vapor flux on all parts of the substrate, or by introducing a gas at a pressure of 5 to 200 μ m into the chamber so that the vapor species undergo multiple collisions during transport from the source to the substrate, thus

producing a reasonably uniform ($\pm 10\%$) thickness of coating on the substrate. The latter technique is called gas-scattering evaporation or pressure plating.

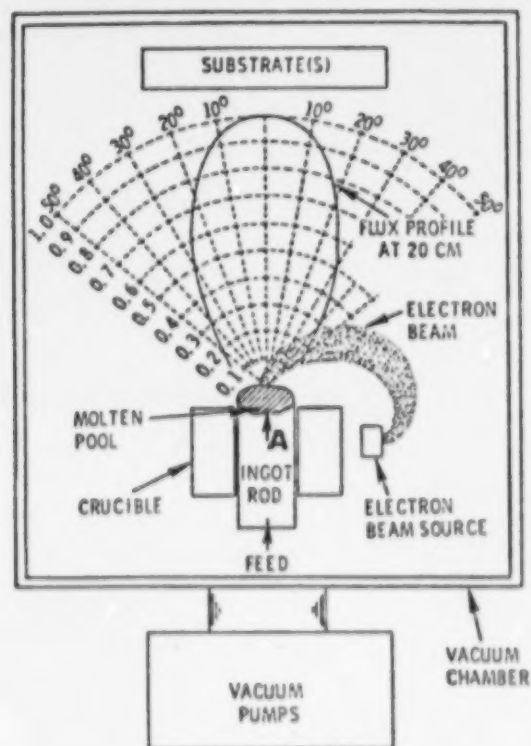


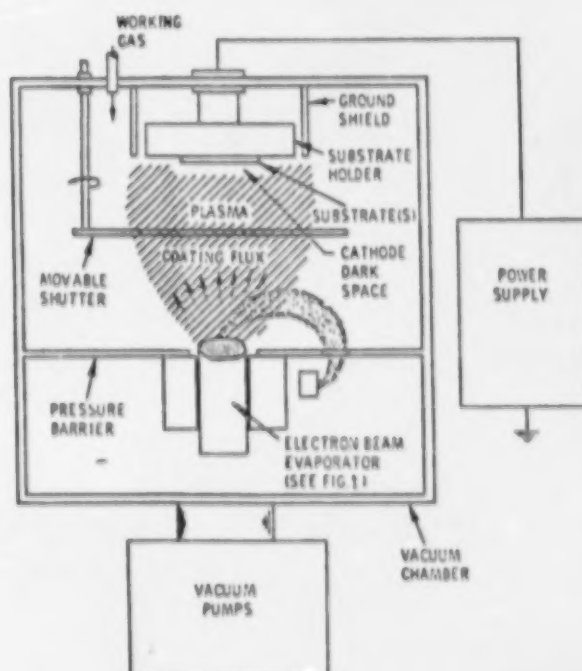
Figure 2. Vacuum evaporation process using electron-beam heating.

Ref. 1

2.2.4 Ion-plating (1)

In the ion plating process, the material is vaporized in a manner similar to that in the evaporation process but passes through a gaseous glow discharge on its way to the substrate, thus ionizing some of the vaporized atoms (see Figure 3). The glow discharge is produced by biasing the substrate to a high negative potential (0.2 to 5 kV) and admitting a gas, usually argon, at a pressure of 5 to 200 μm into the chamber. In this simple mode, which is known as diode ion plating, the substrate is bombarded

by high energy gas ions which sputter off the material present on the surface. This results in a constant cleaning of the substrate (i.e. a removal of gaseous impurities by sputtering) which is desirable for producing better adhesion and lower impurity content. On the other hand, it produces the undesirable effects of decreasing the deposition rates since some of the substrate is sputtered off, as well as causing a considerable (and often undesired) heating of the substrate by intense gas ion bombardment. The latter problem can be alleviated by using the supported discharge ion plating process where the substrate is at a lower negative potential, the electrons necessary for supporting the discharge coming from an auxillary heated tungsten filament. The high gas pressure during deposition causes deposition of all surfaces due to gas scattering as discussed above, although the deposit thickness varies from front to back of the substrate.



Ref. 1

Figure 3. Ion plating process.

2.2.5 Sputtering (1)

In the sputtering process, illustrated schematically in Figure 4, positive gas ions (usually argon ions) produced in a glow discharge (gas pressure 20 to 150 μm) bombard the target material (also called the cathode) dislodging groups of atoms which then pass into the vapor phase and deposit onto the substrate.

The recent development of a class of sputtering sources with magnetic plasma confinement, called magnetrons, and of high performance triodes, is greatly enhancing the capabilities of the sputtering process.

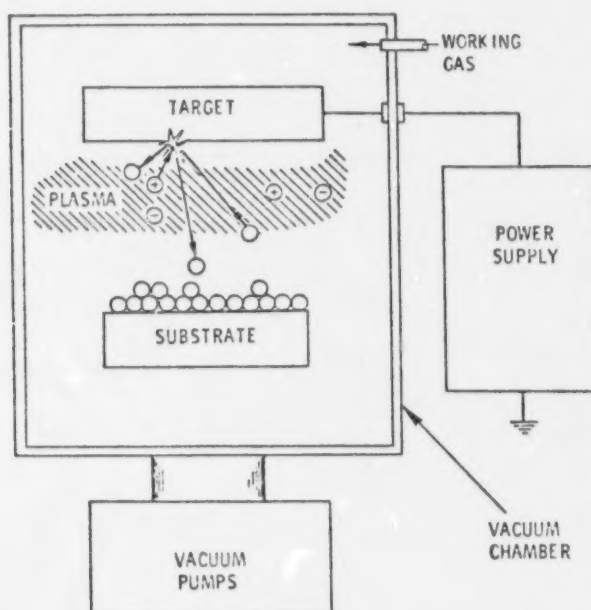
Magnetrons can provide an order of magnitude increase in deposition rate over that of planar diodes. They also can provide uniform deposition over very large substrate areas (many m^2). In addition, well designed magnetrons virtually eliminate substrate heating due to electron and plasma bombardment.

Deposition rates for magnetrons and high performance triodes can be equivalent to those used in electroplating and are high enough to make thick coatings and free standing shapes feasible. For example, high rate triode sputtering has been used to make a free standing 1.3 kg deposit of Cu-alloy in the form of a cylinder 15 cm. in diameter.

Alternate geometries are of importance in various processing applications. For example, the hollow cathode sputtering would be the ideal geometry for coating the outer surface of a wire.

Sputtering is an inefficient way to induce a solid-to-vapor transition. Typical yields (atoms sputtered per incident ion) for a 500 eV argon ion incident on a metal surface are unity. Thus the phase change energy cost is from 3 to 10 times larger than evaporation.

The deposition rates for the various processes are indicated in Table I. It should be noted that sputtering rates at the high side (approximately 10,000 Å/min.) can only be obtained for target materials of high thermal conductivity like copper, since heat extraction from the target is the limiting parameter. For most materials, it is much lower, i.e. 500 to 1000 Å/min.



Ref. 1

Figure 4. Basic sputtering process.

TABLE I

Process	Deposition Rate ($\text{\AA} \text{ min}^{-1}$)
Evaporation	100 - 250,000 (in special cases to 750,000)
Ion Plating	100 - 250,000
Sputtering	25 - 10,000

Ref. 1

2.2.6 Plasma Aided (1)

The adhesion, crystallinity and grain structure of coatings deposited by Physical Vapour Deposition techniques are usually improved if the energy of the depositing particles is increased. Energy can be transferred to the coating atoms by heating the substrate. An alternative method is to increase the kinetic energy of deposition by ionising the vapour atoms and accelerating them in an electric field. A variety of Plasma Aided Techniques had shown that all the improvements brought about by high temperature substrates can be achieved at lower substrate temperatures. The very high ion energies can also cause production of unusual phases and a further advantage is the increased reactivity resulting in deposition of compound coatings.

It is now generally accepted that plasmas can be used in place of substrate temperature in a wide range of deposition processes to improve coating adhesion and structure and to increase reactivity during reactive processes. However, it should be realised that plasma processes can produce very high "equivalent temperatures" in the depositing particles. For example, an ion which has passed through a potential of 100eV has an equivalent temperature of over 1×10^6 °K. This very high energy of deposition allows a new type of film deposition, not possible by conventional thermal or chemical means. As an example of this, by using ion beam or plasma effects carbon coatings have been produced, which are hard, and transparent, and exhibit many diamond like characteristics.

The advantages of Plasma aided technique:

- (a) Good adhesion at low substrate temperatures.
- (b) Good coverage of complicated shapes (and other properties depending on structure).
- (c) Improved structures at low substrate temperatures.
- (d) Enhanced reactivity.

The disadvantages of plasma aided technique:

- (a) The necessity of clamping the sample to a high voltage electrode.

- (b) The necessity of working under a relatively high gas pressure.
- (c) It is difficult to mask parts of the sample.
- (d) The energies of deposition cover a wide range and are difficult to determine or to control.
- (e) The technique is not suitable for coating internal surfaces of tubes.

2.2.7 Thermal Spraying (4)

The two basic processes of spraying materials for high-temperature coatings are flame spraying and arc plasma spraying. Regardless of the process used, spraying involves three stages:

- (1) heating the material to be sprayed to form molten or semimolten droplets in a flame or plasma
- (2) projecting these heated particles at a high velocity onto the part being coated
- (3) the collision of the hot particles with this part, where they adhere to the part to form the final coating.

No other treatment is needed except possibly machining if a smooth surface is desired. The methods whereby the spraying material is supplied to the heating zone of the gun or torch and the methods of heating the material for impingement on the parts are quite diverse.

The spray materials are supplied to the hot zone of the spray gun in wire, rod and powder form. The spray material is fed into a flame or arc for heating and propelled to the object being coated. The flame guns use oxygen as the oxidizer and generally acetylene, hydrogen, or propane, as the fuel, while the arc plasma spray gun generally employs a controlled arc between two electrodes to ionize a flowing gas such as argon or nitrogen, causing a liberation of much heat.

2.2.8 Spray Pyrolysis

Spray pyrolysis is a process whereby a solution of compounds (usually salts) containing the cation(s) and anion(s) of interest is sprayed

onto a hot substrate where the solution components react to form a film or coating of the desired composition. The interesting feature is that the source material is not transported as a vapour but as a solution in droplets. This allows transport at room temperature. When the droplet reaches the heated substrate, the solvent evaporates and a pyrolytic chemical reaction occurs. This process has been used extensively to produce metal oxides from halides or other salts.

Chapter 3 of the review gives a detailed description of the process.

2.2.9 Electrodeposition (4,5)

Electrodeposition is probably the most widely used method of applying a protective metal coating to another material. Hard coatings like nickel and chromium has been applied to various metals by electroplating using aqueous solution techniques. Electrodeposited coatings are more uniform in thickness than hot dipped coatings, less porous the sprayed coatings and of higher purity than either. A further advantage is the close control and wide range of thickness that can be obtained.

The fundamental principles of the process of electroplating are familiar. After a careful cleaning, the article to be plated is made the cathode of an electrolytic cell, i.e. the plating bath, containing in solution a salt of the metal to be electrodeposited as a coating. The anode of this cell is usually formed of the metal to be electrodeposited, but it may be made of another metal or some other highly conducting material such as graphite which is insoluble in the plating bath under the conditions of operation. The plating operation is accomplished by passing a current through this cell, the source of electromotive force being a storage battery, a direct current generator, or a rectified alternating current.

According to Faraday's law the quantity of all of the elements liberated at either the anode or cathode during electrolysis is proportional to the quantity of electricity which passes through the solution. Since at the cathode hydrogen ions as well as metal ions may be discharged, the efficiency of the process of metal deposition may be, and usually is, low.

than 100 per cent. Similarly the dissolution efficiency of the anode may vary from the theoretical maximum to zero depending upon the proportion of the total current entering the solution by dissolution of metal. In certain plating baths, anodes may undergo corrosion of the local action type, in which case the apparent anode efficiency may exceed 100 per cent. With any given plating conditions, the thickness of the deposit is proportional to the period of deposition.

The successful operation of a plating bath requires the control of at least three variables; namely, chemical composition of the plating solution, temperature of solution, and cathodic current density. These variables are related in their effect upon the character of the electrodeposit in such a way that if the range of one is changed it may be necessary to alter the others. Since it is usually desirable in commercial production to employ maximum current densities, it is customary to adjust the bath composition, the temperature, and other factors affecting the plating operation in such a way as to attain this end. Movement of the article being plated or movement of the plating solution with respect to this article generally permits the use of higher current densities.

Cermet Electrodeposition (4)

Electrodeposition of cermets from aqueous solutions has been investigated. The technique of depositing cermets consists of suspending small ceramic particles less than 325 mesh in an agitated electroplating bath. As the metal is deposited, particles are occluded in the deposit. Any combination of an electroplatable metal and particles that do not react with the plating solution can be deposited by this technique.

The particles are maintained in suspension by air agitation or by mechanical stirring. Particle size can range down from about 44 micron size to as small as desired. In most applications, a 3 to 25 micron diameter particles are preferred.

The concentration of particles in a deposit varies with the plating metal matrix, particle size, and the operating conditions of the plating solution, and is limited to about 20 weight per cent when only mechanical agitation is used. However, if the particles are ball-milled with organic additive agents such as zein or benzoic acid prior to their addition to the plating bath, particle concentrations in the metal matrix may be increased.

Metal-ceramic coatings containing a variety of oxide and hard metal particles have been prepared. Nickel, chromium, platinum, rhodium and cobalt-tungsten have been used as the metallic phase.

Cermet deposits suffer from the same drawbacks as many other electro-deposits, i.e. they can be porous and cracked. However, cermet electro-deposits do offer potential in high-temperature applications where the exposure times are short, when erosion conditions are severe, and where a thermal expansion match between a base metal and a pure ceramic outer coat constitutes a problem. The ceramic content of a cermet electrodeposit can be graded from a low to high concentration. Interest in this type of deposition technique is increasing due to the low cost of the process and its adaptability to production.

2.2.10 Anodizing (5,6)

Anodization is a method by which it is possible to increase the thickness of an oxide layer grown on a reactive substrate. The technique is widely used both for research and commercial purposes. Normally the reaction is associated with materials such as aluminum, tantalum, niobium etc. but recently the technique has been extended to the growth of silicon dioxide on silicon carbide by anodization. It has been found that films of silicon dioxide can be grown successfully up to thicknesses of 200Å. The technique has also been applied to the anodization of GaAs. Different electrolytes have been used and the use of H_2O_2 or propylene glycol plus tartaric acid solution buffered by ammonia has been reported (6).

Coatings that provide an insulating barrier of exceedingly low solubility between a metal and its environment through conversion of the metal surface into a corrosion-resistant, nonreactive form play an important role in coating technology. The conversion is a chemical or electrochemical modification of the metal surface so that the coating formed is an integral part of the parent metal. This is in contrast to other coatings which require no chemical combination with the basis metal. Coatings are often absorbent, providing an ideal base for protective oils, waxes, or dyes. Transparent films are used to preserve the optical properties of bright metal surfaces; relatively thick films are effective in improving wear resistance and as an aid in cold forming operations.

Anodic conversion occurs while the part is made the anode in an electrolytic cell. The coatings formed by these methods are principally oxides, in effect "corrosion products" formed under carefully controlled conditions. Through variations in the coating conditions - notably the composition of the treating bath - a wide variety of coating properties can be obtained.

2.2.11 Summary

A general comparison of various hard coatings and surface hardening processes is shown in Table 2.

TABLE 2

Comparison of Various Hard Coatings and
Surface Hardening Processes

Coating Method	Base Metal Temp (C°)	Adhesion	Coverage	Cost	Applicable Coating Material
Chemical Vapor Deposition	975-1050	Superior	Excellent	Normal	Metal, Alloy Carbide Nitride Boride Oxide
Ion Plating	200-500	Excellent	Excellent	High	Metal, Alloy Nitride Carbide
Metal Spraying	150-200	Fair (Fusing Treated. Excellent)	Fair	Low	Metal, Alloy, Oxide
Electrical Plating	Room Temp.-100	Good	Good	Low	Chrome, etc.
Chemical Plating	50-300	Good	Excellent	Normal	Chrome, etc.
Salt & Gas Case Hardening	800-1100	Excellent	Fair	Low	Carbon, Nitrogen, etc.

2.3 Coating Properties

The primary function of a coating is to retard or prevent deterioration of a substrate in service. In order to fulfill this purpose the coating itself must be durable under the service conditions. Not only must it be relatively resistant to corrosion in the service environment, it also must resist mechanical forces such as abrasion, impact or impingements encountered in service. Often there is the added requirement that the coating remain visually attractive throughout its useful service life. The serviceability of a coating thus depends upon its quality in terms of continuity and uniformity, its physical and electrochemical relation to the substrate, the character of the environment to which it is exposed, and the nature of the corrosion products which the coating forms in its chemical reactions with the constituents of that environment.

2.3.1 Appearance

Appearance of the coatings can be revealed by visual examination and by optical microscopy. The visual examination is capable of showing the type of defects as specified in the A.S.T.M. B-532-79. These defects include: cracks, scratches, inclusions, voids, blister, off color, etc.

2.3.2 Thickness

The ASTM standards specify various methods to measure coating thickness. The application of these methods depends upon the properties of coating of interest. These methods are:

(i) Nondestructive Methods

(a) Magnetic Methods

B499-75 Measurement of Coating Thickness by the Magnetic Method: Nonmagnetic Coatings on Magnetic Basis Metals.

B530-75 Measurement of Coating Thicknesses by the Magnetic Method: Electrodeposited Nickel Coatings on Magnetic and Non-magnetic Substrates.

(b) Eddy-Current Method

B244-79 Measurement of Thickness of Anodic Coatings on Aluminum and of Other Nonconductive Coatings on Nonmagnetic Basis Metals with Eddy-Current Instruments.

(c) X-Ray Fluorescence Method

B568-79 Measurement of Coating Thickness by X-Ray Spectrometry.

(d) Beta Backscatter Method

B567-79 Measurement of Coating Thickness by the Beta Backscatter Method.

(ii) Semidestructive Methods

(a) Coulometric Method

B504-70 Measurement of Thickness of Metallic Coatings by the Coulometric Method.

(b) Double Beam Interference Microscope Method

B588-75 Measurement of Thickness of Transparent or Opaque Coatings by Double-Beam Interference Microscope Technique.

(c) Chemical Methods

B555-75 Guidelines for Measurement of Electrodeposited Metallic Coating Thickness by the Dropping Test.

B556-71 Guidelines for Measurement of Thin Chromium Coatings by the Spot Test.

(iii) Destructive Methods

(a) Microscopical Method

B487-79 Measurement of Metal and Oxide Coating Thickness by Microscopical Examination of a Cross Section.

(b) Gravimetric Methods (Strip and Weigh)

A90-81 Tests for Weight of Coating on Zinc-Coated (Galvanized) Iron or Steel Articles.

A309-81 Test for Weight and Composition of Coating on Long Terne Sheets by the Triple Spot Test.

A630-68 Determination of Tin Coating Weights for Hot-Dip and Electrolytic Tin Plate.

B137-45 Measurement of Weight of Coating on Anodically Coated Aluminum.

2.3.3 Adhesion

The ASTM B-571-79 Standard describes several methods for evaluating the adhesion of coatings on various substrates. The methods are qualitative and require only simple tools or instruments and moderate skill.

Several of the tests are limited to specific type of coatings, thickness ranges, ductilities, or compositions of the substrates.

"Perfect" adhesion exist if the bonding between the coating and the substrate is greater than the cohesive strength of either. Such adhesion is usually obtained if good coating practices are followed. For many purposes, the adhesion test has the objective of detecting any adhesion less than "Perfect". For such a test, one can use any means available to attempt to

separate the coating from the substrate. If the coating peels, flakes or leaves from the substrate, the adhesion is less than perfect. These methods include:

- (1) Bend test
- (2) Burnishing test
- (3) Chisel Knife test
- (4) Draw test
- (5) File test
- (6) Grind Saw test
- (7) Heat Quench test
- (8) Impact test
- (9) Peel test
- (10) Push test
- (11) Scribe Grid test

For details of each method, see the ASTM B-571-79.

2.3.4 Microstructure

Film morphology can be examined by optical microscopy (O.M.) and scanning electron microscopy SEM. The SEM has a high depth of field which gives a better resolution on coating morphology.

The microstructure of the coatings can also be examined by O.M. and SEM. Hard coatings require special care for metallographic preparation to minimize the interruption of the coating interface. Sometimes, a fractured specimen is used for the SEM examination.

2.3.5 Hardness

Coating hardness due to the limitation of thickness should be measured by a microhardness tester. The ASTM B-578-80 specifies standard test method for "Microhardness of Electroplated Coatings". The measurements are made with the Knoop indenter under a test load of 25 g or 100 g. The

method shall be performed in accordance with Method ASTM E-384-73. The measurement shall be made on the cross section with long diagonal of the indentation parallel to the substrate using a Knoop indenter. The thickness of coating shall be at least 25 μm for hard coatings. This is approximately equivalent to 0.6 times the length of the long Knoop diagonal. A load of less than 25 g is not recommended. The Knoop hardness makes decreases appreciably with loads from 25 gm to 100 gm especially for high hardness number.

2.3.6 Abrasion Resistance

There are a full list of abrasion resistance testing methods in the ASTM Standard. The application of each method to the coatings is limited to the type of coating materials, the degree and the condition of the abrasion resistance, the thickness of the coatings, the adherence of coatings to substrate and the physical size and properties of the coated substrate. The following is a list of abrasion resistance testing methods which shows potential interest for evaluation of wear resistant coatings:

(i) Sand Blaster Methods

- C-418-81 Abrasion Resistance of Concrete by Sandblasting
- C-158-80 Flexure Testing of Glass
- D-658-81 Abrasion Resistance of Organic Coating by Air Blast Abrasive.
- D-968-81 Abrasion Resistance by the Falling Abrasive Tester
- D-4060-81 Abrasion Resistance of Organic Coatings by Taber Abraser.
- D-704-76 Abrasion Resistance of Refractory Material at Room Temperature.

(ii) Taber Abraser Methods

- C-501-80 Relative Resistance to Wear of Unglazed Ceramic Tile by Taber Abraser
- F-510-81 Resistance to Abrasion of Resilient Floor Coverings Using the Taber Abraser with Trick Grit Feed Method.

(iii) Rotating Cutter Methods

- C-944-80 Abrasion Resistance of Concrete or Mortar Surfaces by the Rotating-Cutting Method.
D-2228-69 Rubber Property - Abrasion Resistance (Pico Abrader).

(iv) Sliding Methods

- C-779-81 Abrasion Resistance of Horizontal Concrete Surfaces
C-448-81 Abrasion Resistance of Porcelain Enamels
D-1630-61 Rubber Property Abrasion Resistance (NBS Abrader)
B-611-76 Abrasion Wear Resistance of Cemented Carbides
F-735-81 Abrasion Resistance of Transparent Plastics and Coatings Using the Oscillating Sand Method

(v) Scratch Methods *

CGSB 1-GP-71 Method 116.2-1974 Scratch Resistance

* Not ASTM STANDARD

2.3.7 Corrosion Resistance

A perfect coating has corrosion resistance properties equivalent to the coating material. Generally, the coating material is more corrosion resistant than the substrate material. Poor corrosion resistance of the coating is the result of the coating defects: such as cracks, porosity, uncoated area, poor coating adhesion etc. The medium used for the corrosion resistance evaluation should attack the substrate material but not the coating material.

There are many ASTM standard methods to evaluate corrosion resistance of coatings. The most common methods are:

(i) Atmospheric Methods

- B 117-73 Salt Spray (Fog) Testing
- G-7-77 Atmospheric Environmental Exposure Testing of Non-metallic Materials
- G-50-76 Atmospheric Corrosion Tests on Metals

(ii) Immersing Methods

- G-31-79 Laboratory Immersion Corrosion Testing for Metals
- G-52-76 Surface Seawater Exposure Tests on Metals and Alloys

(iii) Electrolytic Methods

- B-627-79 Electrolytic Corrosion Testing
- G-71-81 Conducting and Evaluating Galvanic Corrosion Tests in Electrolytes

(iv) High Temperature Oxidation Method

- G-54-77 Simple Static Oxidation Testing

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2.4 Tin (IV) Coatings

Tin oxide coatings on glass or ceramic substrates are prepared by a wide variety of techniques for very diverse applications. The three primary applications of tin oxide coatings are:

- "hot end" coated glass ware for improved strength and abrasion resistance.
- visibly transparent, infrared reflecting "heat barrier" coatings.
- visibly transparent, electrical conductors for optical/electronic applications.

The requirements of the application often dictate the application method to be used. Of particular concern are:

- substrate material
- substrate size
- temperature limitations
- desired film properties
- cost

Tin oxide coatings are applied to bottles as a "hot end" coating to increase glass strength, reduce abrasion during handling and reduce the coefficient of friction between treated bottle surfaces. These coatings are usually applied by the spray pyrolysis or vapour pyrolysis method ⁽¹⁾ (see Section 2.2).

"Heat barrier" coated glass using doped tin oxide or indium/tin oxide (ITO) be commercially available for many years ^(2,3).

It is generally agreed that SnO_2 in its undoped form is an n-type, wide-bandgap semiconductor. Various specific and unique properties of this material make it very useful in many applications. Polycrystalline thin

films and ceramics of SnO_2 have been extensively used for the production of resistors ⁽⁴⁾. Conducting SnO_2 films are well known as transparent electrodes, and when deposited on glass it is known as Nesa glass ⁽⁵⁾. SnO_2 films are also used as transparent heating elements ⁽⁶⁾, for the production of transistors ^(7,8), for transparent antistatic coatings ⁽⁹⁾, and other parts in electric equipment where transparency is required. A polarized memory effect has also been observed in a Se- SnO_2 system ⁽¹⁰⁾.

Because of its practical importance, an increasing amount of work has been done on crystals and films in recent years. A great deal of experimental research has been carried out on the electrical and optical properties of single crystals, thin films, and sintered SnO_2 in the hope of gaining a detailed understanding of the semiconducting nature of this material. Parallel to the electrical and optical work performed, there is considerable industrial activity regarding SnO_2 films on bottles and especially in the area of organic or silane coatings used in conjunction with the SnO_2 layer to reduce bottle abrasion ^(11,12,13,14,15,16,17,18,19).

2.4.1 Preparation

As mentioned previously, the coating application technique is usually geared to the application. Hot end coatings of container glass with SnO_2 (although sometimes TiO_2 is used) is accomplished by the decomposition or hydrolysis of tin compounds to form SnO_2 . Usually SnCl_4 is used although organotin compounds and SnCl_2 have been used. Hot end coatings are applied after the containers leave the forming machine and before they enter the annealing lehr. The cold end coatings are applied after the annealing lehr. It is believed that the best scratch resistance occurs when a hot end coating of tin or titanium oxide is used in conjunction with a long chain fatty acid cold end coating ⁽¹⁹⁾, although various organic materials have been used, such as, waxes, polyethylene, oleic acid, stearates, polyethylene glycol, octadecylamine ^(16,20,21,22).

The various processes used to prepare SnO_2 films for electrical and optical applications have been reviewed by Jarzebski and Marton ⁽²³⁾ and some results are listed in Table 2.4.1.

TABLE 2.4.1 (23)

Deposition of SnO_2 Films

Year	Author	Reference	Method
1953	Holland and Siddal	(9)	Reactive sputtering of Sn cathode
1954	Aitchison	(5)	Hydrolysis of SnCl_4 on heated glass substrate based on reaction $\text{SnCl}_4 + 2\text{H}_2\text{O} \rightleftharpoons \text{SnO}_2 + 4\text{HCl}$ at temperature range 770°-1070°K
1958	Ishiguro, Sasaki, Arai, and Imai	(35)	Solution of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ crystal or SnCl_4 liquid in distilled water or in ethyl alcohol was sprayed on the glass, fused silica, or rock salt plates at temperatures 770°-870°K. The obtained SnO_2 films were comprised of crystallites.
1960	Arai	(35)	(i) Hydrolysis of SnCl_4 (ii) Heating with air the SnO films obtained by vacuum evaporation of SnO powder
1960	Kuznetsov		Hydrolysis of SnCl_4 without intentional doping
1963	Koch		Hydrolysis of SnCl_4
1963	Sinclair and Peters		Reactive sputtering of Sn cathodes
1964	Maesen and Witmer	(6)	Hydrolysis of SnCl_4
1964	Klaassen and Koeimans	(7)	Vacuum evaporation process
1965	Sinclair, Peters, Stillinger, and Koonce	(41)	Reactive sputtering of Sn cathode
1965	Vainshtein	(42)	Reactive sputtering of Sn cathode
1965	Tigane	(43)	Pyrolysis
1966	Sasaki, Nishimura, and Yamamoto	(44)	Hydrolysis of SnCl_4
1966	Shiojiri Morikawa, and Suito	(45)	Vacuum evaporation of SnO_2
1967	Spence	(46)	Vacuum evaporation of tin in oxygen atmosphere
1969	Bartholomew and Garfinkel	(47)	Producing SnO_2 films on silica glass substrate by oxidation of SnCl_4
1969	Victrian and Georgescu	(48)	SnO_2 films prepared using anhydrous tin chloride in alcohol
1969	Inagaki, Nishimura, and Sasaki	(49)	Droplet gas-phase reaction
1969	Časlavská and Roy	(21)	Epitaxial growth of SnO_2 films on rutile single crystal using reaction $\text{SnI}_4 + 2\text{H}_2\text{O} \rightleftharpoons \text{SnO}_2 + 4\text{HI}$
1969	Lieberman and Modrud	(50)	Reactive sputtering of Sn electrode
1969	Yamanaka and Oohashi	(51)	Reactive sputtering of SnO_2 itself
1970	Elliott, Zellmer, and Laitinen	(52)	Hydrolysis of solution of acidified SnCl_4 containing various percentages of SnCl_4 on a hot substrate (Pyrex, quartz, or polished platinum)
1970	Aoki and Sasakura	(8)	SnO_2 thin films were grown by transporting the vapor of $(\text{CH}_3)_2\text{SnCl}_2$ onto the substrate with dried air and by decomposition and oxidizing
1970	Nishino and Hamakawa	(53)	Conductive SnO_2 films were obtained by two processes: (i) evaporation of tin on silicon and (ii) oxidation of these films at temperature range 570°-870°K for several minutes
1971	Vorob'eva and Polurotova	(54)	Hydrolysis of SnCl_4 without intentional doping
1972	Hecq and Portier	(55)	Reactive sputtering of Sn cathode
1972	Vossen and Poliniak	(56)	RF sputtering very thin films of $\text{SnO}_2:\text{Sb}$ and $\text{In}_2\text{O}_3:\text{Sn}$
1973	Kelly and Lam	(57)	Reactive sputtering of Sn cathode
1973	Abouaf and Marcotte	(58)	Hydrolysis of SnCl_4
1974	Giani and Kelly	(59)	(i) Reactive sputtering of Sn cathode (ii) Anodizing of Sn in electrolyte of ammonium pentaborate in ethylene glycol with water
1974	Lepic and Marton	(60)	Hydrolysis of SnCl_4 on ceramic substrate. The films of $\text{SnO}_2:\text{B}:\text{Sb}$ were obtained by adding H_3BO_3 or SbCl_3 to the solution

The current interest in optical and electrical applications of tin oxide films has led to more careful study of the techniques which can be employed to deposit these films and also to study the dependence of SnO_2 films on the mode of preparation.

As can be seen from Table 2.4.1 many methods have been used to obtain SnO_2 thin films; however at present it seems that only two of them are promising for future development. These are gas-phase hydrolysis of volatile tin compounds, principally SnCl_4 using various carrier gases, and reactive sputtering.

The method of hydrolysis is based on the reversible endothermic reaction in the presence of HCl gas. Because this reaction proceeds very rapidly, the SnCl_4 is mixed with alcohol, some organic acid, or both. When spraying an atomized mixture of this solution onto a heated substrate, the reaction occurs in the forward direction resulting in the deposition of tin oxide in the form of a smooth, closely adherent transparent film. The reaction proceeds slowly at 770°K , and is very rapid at temperatures higher than 1070°K . If the temperature of the substrate is higher than about 1270°K , metallic tin is formed. The optimum temperature range for SnO_2 film formation appears to be different in the experience of different workers. Aboaf and Marcotte claim good results in the temperature range of 650°K - 870°K , while other authors prefer temperatures of 770°K - 870°K and 770°K - 1070°K .

An analysis of the SnO_2 films obtained in this way suggests contamination of chlorine and deviation from stoichiometry. Cl contamination and oxygen deficiency are responsible for the rather high conductivity found in these films which are made without intentional doping. Usually, however, high conductivity tin oxide films are obtained by doping them with antimony, boron, or other elements such as FeP. To obtain SnO_2 films doped with antimony or boron, various percentages of SbCl_3 (or SbCl_5) or H_3BO_3 are added to the acidified-atomized solution of SnCl_4 .

Because the reaction is reversible the structure and composition of SnO_2 films depend on the temperature, pressure, and rate of deposition. The tin oxide films can be obtained clear and virtually insoluble in acids and bases. The chlorine content was lowest when the films were deposited in a hydrogen atmosphere. SnO_2 films prepared by the method of hydrolysis of SnCl_4 exhibit a small temperature coefficient of resistivity and are chemically stable at slightly elevated temperatures, but they are polycrystalline.

Reactive sputtering has been used to produce SnO_2 and doped SnO_2 coatings using a Sn (or doped Sn) cathode in a low pressure O_2 containing

environment. SnO_2 sintered cathodes have also been used.

Anhydrous SnCl_2 has been used as a starting material for preparing SnO_2 films. Stannous chloride with the melting point of 519°K was fused and subsequently oxidized to SnO_2 by the following reaction:



SnO_2 films have been prepared by transporting dimethyl tin dichloride $(\text{CH}_3)_2\text{SnCl}_2$ vapor onto a substrate surface by means of dried air, where the vapor was successively decomposed and oxidized. The thickness of the SnO_2 films was controlled by changing the flow rate of the air and the time of reaction, and their electrical conductivity was controlled by changing the temperature of the substrate.

Conductive tin oxide films have been grown by the evaporation of tin on a suitable substrate and the subsequent oxidation in an atmosphere containing oxygen.

SnO_2 films have also been prepared by a high voltage anodizing method. The anode was an Sn sheet and the cathode was either an Al sheet or a Pt cylinder. The electrolyte used was an ammonium pentaborate in ethylene glycol which was varied by adding water.

A large number of patents have been issued for solutions, reagents, application machinery and uses of SnO_2 (usually doped) films.

2.4.2 Properties

Film properties are generally a function of application conditions and technique. Most of the literature and patent information is directed towards electrical and optical properties which are not of primary interest here. Reviews of the electrical⁽²⁴⁾ and optical⁽²⁵⁾ properties of SnO_2 films have been compiled by Jarzebski and Marton. Comprehensive studies of SnO_2 films have been carried out by Aitchison⁽²⁶⁾. He found that stoichiometric tin oxide films have a high resistivity (about 10^8 ohm-cm)

at room temperature. The addition of atoms with a valence higher than four, e.g. Sb, has a similar effect to the reduction of SnO_2 films and causes a significant increase in conductivity. The addition of fluorine as a substitute for oxygen also results in very good conductivities.

The general range of reported film properties is qualitatively presented in Table 2.4.2.

The adherence of the films was reported to be good on glassy, or oxide and silicate crystal substrates but poor on ionic halide crystals and metals.

2.4.3 Applications

Transparent semiconducting tin oxide has recently gained prominence in the manufacture of transparent electrodes for heterojunction solar cells. In addition, it has a refractive index in the range 1.8-1.9, making it suitable as an inherent antireflection coating on silicon.

Transparent semiconducting SnO_2 has been used for "heat barrier" oven windows, antifrost windshields, reduced emissivity coatings on black enamels for solar absorbers, antistatic coatings and in the manufacture of thin film resistors.

Tin oxide is used extensively as a "hot end" coating in conjunction with a "cold end" organic coating to increase the strength and abrasion resistance of glass containers.

Several methods which have been developed to obtain suitable conductive SnO_2 layers.

Suppering methods (r.f. or d.c., reactive or non-reactive) produce high quality films but the apparatus required is expensive and their low production rate makes them less useful for mass production. Sputtered films usually need further annealing to stabilize their characteristics.

TABLE 2.4.2

Typical Film Properties for SnO₂

Material	SnO ₂
Dopant	Sb, In, P, F,
Thickness	0.01 μ to 1.0 μ
Physical properties	- close or equivalent to SnO ₂
Grain size	1 - 100 Å
Sheet Resistivity	10 - 10000 Ω /square (doped)
Bulk Resistivity	1 x 10 ⁻³ Ω cm (doped)
Adhesion	oxides: good to excellent metals: not good adherence ionichalides: not good adherence
Optical	60 - 80% (some haze is possible)
Transmission	(interference rings on thicker coatings)
IR Reflectance	40 - 80%
Coefficient of friction	0.2 - 0.7 (depending on film, heat treatment and other coatings)
Common application	spray pyrolysis of SnCl ₄
Methods:	CVD of SnCl ₄ , organotin spray pyrolysis of SnCl ₂ sol-gel coating.

Evaporation methods employ either an electron beam or flashing to evaporate the material. They have the same disadvantages for mass production as sputtering methods.

Precipitation from a solution of SnCl_4 and water can be used to prepare films of SnO_2 . Annealing at 500°C is usually necessary to lower the film resistivity and to stabilize its characteristics. No method has been devised to control the thickness of the deposited film.

Chemical vapour deposition methods produce good quality films. Organometallic compounds are usually employed as the reactants. The deposition set-up is rather too expensive to allow mass production of these films for solar energy applications.

Spraying methods are based on the pyrolytic decomposition of tin compounds dissolved in a liquid mixture sprayed onto a previously heated substrate.

The simplicity of the deposition apparatus allows for the mass production of doped SnO_2 films. The resulting films are fairly uniform, with resistivities ranging between 10^{-2} and $8 \times 10^{-4} \Omega\text{cm}^5$ and optical transmittances around 80% in the visible region and good reproducibility.

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2.5 Alumina Coatings

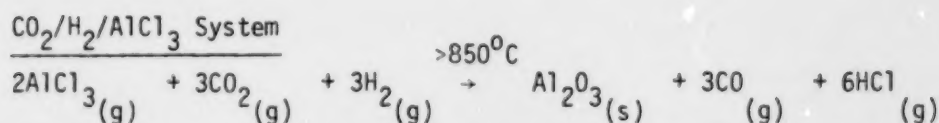
2.5.1 Preparation

There are various methods for formation of aluminum-oxide coatings. The films obtained at temperature range of 400-600°C are amorphous^(2-8, 13), and films obtained at 850°C^(1,7-12, 14) and above are polycrystalline aluminum oxide.

2.5.1.1 Chemical Vapour Deposition

(a) Hydrolysis of AlCl_3 ^(1,9-14)

Among the different conventional systems possible to use for depositing Al_2O_3 coatings, the $\text{H}_2\text{O}/\text{AlCl}_3$ systems seems to be too reactive^(12,18,19) whereas the O_2/AlCl_3 system is almost non-reactive⁽¹⁹⁾. The $\text{CO}_2/\text{H}_2/\text{AlCl}_3$ ^(11,12) system was found to be more easily controlled than the $\text{H}_2\text{O}/\text{AlCl}_3$ system. The reactions taking place in a low pressure system (Figure 1) are the following⁽¹²⁾:



The influence of temperature on the deposition rate of the two systems is shown in Figures 4 and 5⁽¹²⁾.

The influence of the total gas pressure and the nature of the gas mixture on the deposition rate of the $\text{CO}_2/\text{H}_2/\text{AlCl}_3$ system is shown in Figures 6 and 7⁽¹²⁾.

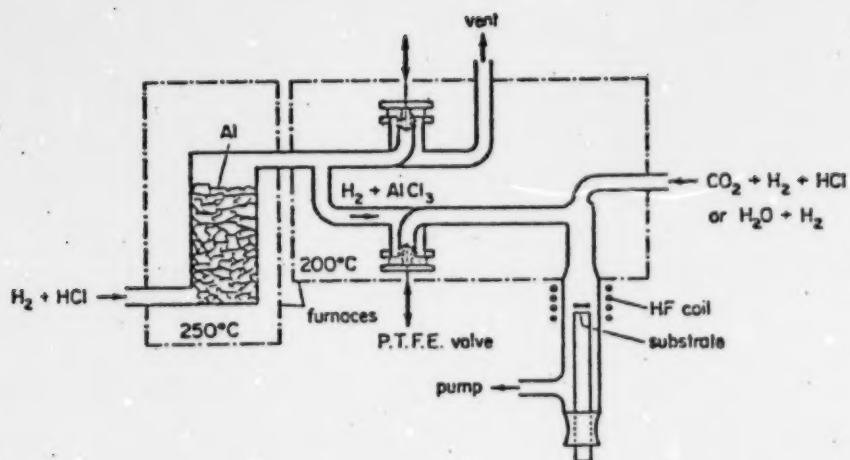


Fig. 1. Apparatus for chemical vapor deposition of Al_2O_3 (schematic).

Reference 12

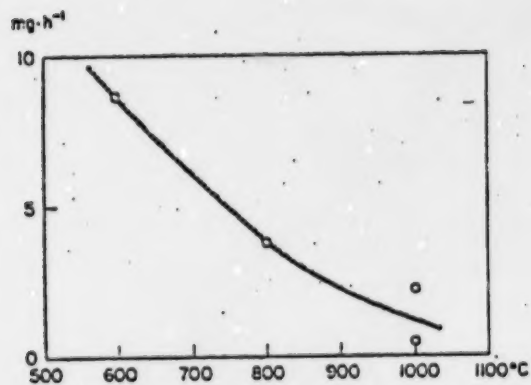


Fig. 4. H_2O -process: Deposition rate as a function of substrate temperature (substrate: ISO P30, total pressure: 5 Torr, partial pressures: AlCl_3 -0.02, H_2O -0.06, H_2 -4.92 Torr; linear gas velocity at 200 $^{\circ}\text{C}$: 9.4 $\text{cm}\cdot\text{sec}^{-1}$).

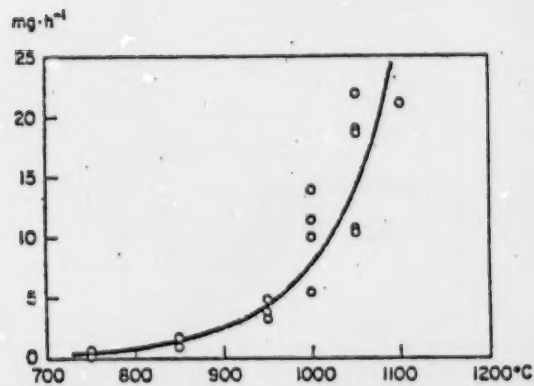


Fig. 5. H_2 - CO_2 process: Deposition rate as a function of substrate temperature (substrate: ISO P30, total pressure: 50 Torr, partial pressures: AlCl_3 -0.2, CO_2 -24.9, H_2 -24.9 Torr; linear gas velocity at 200 $^{\circ}\text{C}$: 9.4 $\text{cm}\cdot\text{sec}^{-1}$).

bombardment of the substrates, increased as the deposition rate increased since the anode was not cooled. A range of 100° – 600°C was observed. Depending on the experimental conditions, two types of alumina films could be deposited. A polycrystalline α -alumina film resulted under conditions favouring high deposition rates and substrate temperatures. At low deposition rates (below $400 \text{ \AA}/\text{hrs}$ and substrate temperatures (100 – 600°C), an amorphous alumina film was deposited.

2.5.1.3 Reactive Evaporation⁽⁶⁾

Ferrier⁽⁶⁾ reported that an amorphous alumina film had been vacuum deposited on silicon substrates by reactive evaporation though a highly localized partial pressure of water vapour at temperature under 300°C . Schematic of the vacuum deposition system is shown in Figure 3.

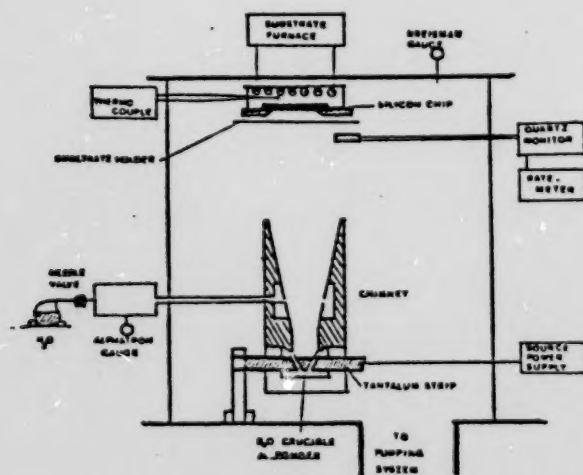


Fig. 3. Schematic of the vacuum deposition system

Ref. 6

The reactive evaporation of aluminum oxide was performed as follows:

1. A silicon substrate was plated at the top of the vacuum jar (Figure 1) and outgassed under vacuum at 450°C for 2 hrs using a radiative furnace placed above it. The substrate temperature was between room temperature and 300°C . The vacuum system was at 5×10^{-6} Torr.
2. Very pure aluminum powder (99.999%) was evaporated from a beryllium crucible heated by a tantalum strip.
3. Water vapour was injected into the vacuum system through a needle valve. The reaction between the evaporated aluminum particles and the water vapour was confined in a chimney in order to maintain a high concentration of water vapour only in the evaporation field. The pressure in the vacuum system was 4×10^{-4} Torr.
4. A shutter was open, and the oxidized aluminum was allowed to be deposited on the silicon substrate. Deposition rates of aluminum oxide were 4 to $20\text{\AA}/\text{S}$. After deposition, the layer was annealed for $\frac{1}{2}$ hour at 300°C .

Adhesion of the alumina layer to the silicon substrates was reported to be excellent for films with thickness up to $20,000\text{\AA}$ operating at substrate temperatures in excess of 100°C .

2.5.1.4 Anodizing of Aluminum in Oxygen Plasma⁽⁵⁾

Waxman⁽⁵⁾ reported that Al_2O_3 films were formed by first depositing aluminum on freshly cleaned silicon and then anodizing the aluminum in an oxygen plasma. The sample was annealed for 1 hr at 300°C in an inert (N_2 , He) ambient atmosphere. The alumina film produced is amorphous. The fibre thickness is between 500 and $700\text{\AA}$.

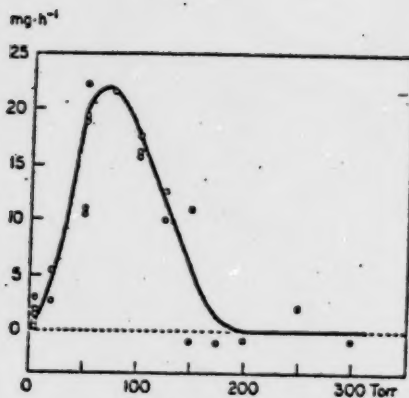


Fig. 6. H_2 - CO_2 process: Deposition rate as a function of total pressure at constant mass flow rate (substrate: ISO P30, substrate temperature: 1050°C , gas composition: AlCl_3 -0.4%, CO_2 -49.8%, H_2 -49.8%; linear gas velocity at 50 Torr and 200°C : $9.4 \text{ cm}\cdot\text{sec}^{-1}$).

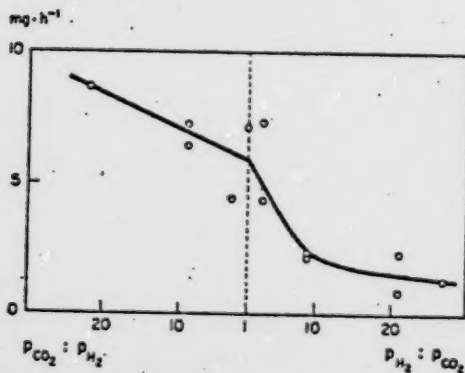


Fig. 7. Deposition rate as a function of $P_{\text{CO}_2}:P_{\text{H}_2}$ and $P_{\text{H}_2}:P_{\text{CO}_2}$ (substrate: ISO P30, substrate temperature: 1000°C , total pressure: 50 Torr; P_{AlCl_3} : 1.5 Torr; linear gas velocity at 200°C : $9.4 \text{ cm}\cdot\text{sec}^{-1}$).

(b) Pyrolysis of Organic Aluminum Compounds
 (e.g. $\text{Al}(\text{C}_3\text{H}_7\text{O})_3^{(2,3)}$, $\text{Al}(\text{C}_2\text{H}_5\text{O})_3$)

Amorphous aluminum oxide films can be deposited at $400\text{--}450^\circ\text{C}$ by thermal decomposition of an aluminum alkoxide (e.g. $\text{Al}(\text{C}_3\text{H}_7\text{O})_3^{(2,3)}$, $\text{Al}(\text{C}_2\text{H}_5\text{O})_3^{(4)}$). A typical schematic of the apparatus of the system is shown in Figure 2⁽²⁾. The reducing or oxidizing atmosphere used (N_2 , H_2 or O_2) during deposition affects the chemical and electrical properties of the oxide film.

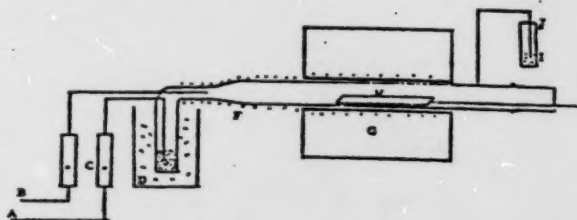


Fig.2: Schematic of apparatus for deposition of Al_2O_3 films: A, dry N_2 ; B, dry N_2 , O_2 , or $90\text{N}_2 + 10\text{H}_2$; C, flowmeters; D, constant temperature bath; E, aluminum tri-isopropoxide; F, heating mantle; G, tube furnace; H, substrate holder; I, oil bubbler; J, exhaust.

Ref.2

2.5.1.2 Reactive Sputtering (7,8)

Frieser⁽⁷⁾ reported that a thin Al_2O_3 film was prepared on a silicon disk by reactive sputtering under a reduced pressure (O_2 or O_2/Ar mix) system. The anode, which held the materials to be coated, was above the cathode which held a disk of pure aluminum. The deposition film thickness is in the range of $500\text{--}7000 \text{ \AA}$. The deposition rate of the reactively sputtered alumina was found to vary directly with the sputtering voltage ($1\text{--}2 \text{ kV}$), the total sputtering gas pressure ($1 \text{ to } 5 \times 10^{-4} \text{ Torr}$), the current density ($0.25\text{--}3.5 \text{ MA/cm}^2$) and inversely with the electrode separation ($2.5\text{--}5.0 \text{ cm}$). The deposition, however, was found to decrease as the oxygen partial pressure increased in an oxygen-argon mixture of the sputtering gas. The substrate temperature, as a result of the ion and electron

2.5.1.5 Sol Gel Method^(14,15)

Yoldas reported the formation of porous transport Al_2O_3 from aluminum alkoxide by the sol-gel method. Sol-gel alumina coatings can be supplied on various glass and ceramic substrates^(20,22). The process of making transparent monolithic alumina involves:

1. Hydrolysis of aluminum alkoxides
2. Peptization of the hydroxide to a clear sol
3. Gel formation
4. Pyrolysis to alumina

2.5.1.6 Spray Pyrolysis⁽²¹⁾

Blandenet⁽²¹⁾ has briefly mentioned as aluminum oxide coating produced by the pyrosol process (spray pyrolysis). Aluminum isopropoxide in butanol was sprayed at a reaction temperature of $650^{\circ}C$ on glass substrate to produce aluminum oxide coating. No further details or references were given.

2.5.2 Properties

2.5.2.1 Amorphous Al_2O_3

Amorphous Al_2O_3 coatings have been used as insulating layers in the semiconductor and transistor industry.

The coatings have the following properties:

1. dense and free of pin holes
2. homogeneous and uniform in thickness
3. chemically inert and easily etchable
4. with surface passivating properties
5. as a diffusion barrier against sodium and hydrogen⁽⁴⁾
6. superior moisture resistance compared to SiO_2 films deposited at comparable temperatures
7. high dielectric strength over 3×10^5 V/cm⁽²⁾
8. high thermal conductivity ($0.081 \text{ cal/cm.s } ^{\circ}C$)⁽¹¹⁾
9. resistant to thermal shock

10. with a thermal expansion coefficient matching that of the substrate to achieve better adherence
11. with polarization effect⁽⁴⁾.

2.5.2.2 Polycrystalline α - Al_2O_3

Polycrystalline alumina is a hard refractory material which has been used as a wear resistant coating on cutting tool bits. The α - Al_2O_3 coating has the following characteristics^(1,7-12,13):

1. very hard refractory material with Vicker's hardness at 3000
2. dense
3. high melting point 2018°C
4. high abrasion resistance
5. inert and stable at working conditions
6. minimum heat absorption
7. thermal expansion coefficient matching with that of the substrate to have good adherence.

2.5.3 Applications

2.5.3.1 Insulating Layers on Semiconductor Surface

Amorphous Al_2O_3 thin film can be deposited and used as insulation layers on semiconductor surfaces^(17,2,5). Applications of Al_2O_3 for passivation of the device⁽⁷⁾ and for fabrication of MOS transistors⁽⁵⁾ and thin film transistors are known. (The combination of Al_2O_3 deposited over SiO_2 will have particularly desirable characteristics for semiconductor technology). The Al_2O_3 film is superior to SiO_2 film alone. It is far less susceptible to hydration and much more stable under bias-temperature stress than the SiO_2 coating.

2.5.3.2 Wear Resistant Coatings on Cutting Tool Inserts

The improvements achieved by thin layers of wear resistant coatings seem to be caused by the retardation of chemical processes contributing to

the wear, especially diffusion and oxidation. In the case of uncoated tool tips the workpiece tends to react by forming alloys with the cemented carbide binder (cobalt alloy) at high cutting temperatures (about 1000°C). Therefore, the chemical resistant oxide layers, e.g. Al_2O_3 ought to be even more suitable for this application than carbides and nitride e.g. TiC , TiN ⁽¹¹⁾. Al_2O_3 coatings with a thickness as low as 1 μm have been effective⁽¹²⁾.

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2.6 Zirconia Coatings

2.6.1 Preparation

2.6.1.1 Thermal Spraying

(a) Plasma-Arc Spraying

Kawabuchi and Magari ⁽¹⁾ reported the deposition of crystals from plasmas of ZrO_2 , HfO_2 , ThO_2 and CeO_2 onto a cathode made of tantalum metal. For the deposition of zirconia coatings powder of ZrO_2 (99.99%) purity was used as a starting material. This powder was pressed in a steel die 12mm in diameter at 2.4 T/cm^2 into a hollow cylinder. The cylinder was sintered at 1500°C for 1 hour in a vacuum of 1×10^{-5} Torr. The Final cylinder was 11mm in outside diameter, 5.5mm in inside diameter and 12mm high.

A schematic diagram of the plasma current is shown in Figure 1.

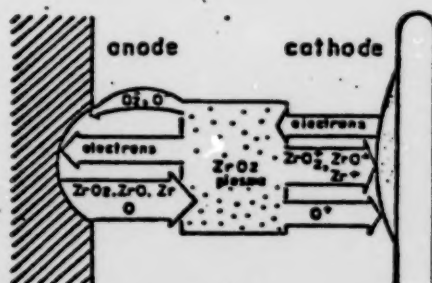


FIG. 1. The schematic diagram showing the three elemental currents of a plasma current—an electron current, a current of ion species containing a metal atom, and a current of O^+ .

From ref. 1

(b) Flame Spraying

Buckley ⁽³⁾ reported the flame spraying and plasma spraying of two zirconia coatings and a zirconia-nickel aluminide cermet coating on Ni-Mo-C metal.

The metal substrates were sandblasted with 120 grit aluminum oxide and cleaned with methyl ethyl ketone. Stabilized zirconia rod was used for the flame spraying. Coating was done in a water-wash spray booth. Flame spraying was accomplished by feeding a 3/16 in. zirconia rod, partially stabilized with calcia, into an oxyacetylene air flame. The spray gun was passed by hand over the specimens at a distance of approximately 4 in.

Zakharov and Trofimov (4) reported the deposition of zirconia coatings on 1 Kh18N9T steel specimens using an oxyacetylene torch. The temperature in the centre of the gas stream was 2200°C . Specimen heating time was 30 s. Zirconium dioxide rods with alumophosphate binder additions were used for this gas-flame spraying process. Spraying was also carried out on glass.

The deposition from the oxide plasma onto a cathode was examined by varying the plasma current and the cathode heating power, and by feeding Ar and O_2 gases into the oxide plasmas. Figure 2 shows the relationship between the plasma current and temperature of a ZrO_2 deposit.

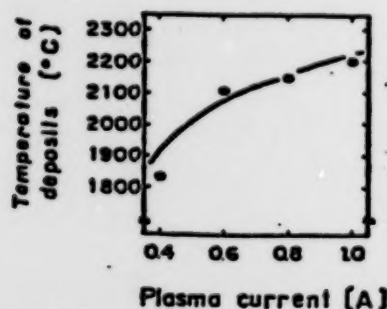


FIG. 2. The relation between the plasma current and the temperature of a ZrO_2 deposit.

From Ref. 1

The pressures of Ar and O_2 were increased from 1×10^{-6} Torr up to 8×10^{-3} and 6.5×10^{-4} Torr, respectively. The deposition time was fixed at 4 min.

Nicoll et al. (2) reported an air-plasma sprayed (Ni-Cr-Al-Y)/ $\text{ZrO}_2\text{-Y}_2\text{O}_3$ duplex coating for use in high temperature reactors to improve the wear resistance.

The layers were applied in two stages to cleaned and roughened IN 625 substrates using a Plasmadyne system. A total energy of 19 kW was used for each layer and cooling of the substrates was not necessary. All spraying was carried out in air using argon as the plasma gas and an internal

powder feed. The particle size of the Ni-Cr-Al-Y powder was $-200 + 325$ mesh and that of the $\text{ZrO}_2\text{-Y}_2\text{O}_3$ was $-45 + 22.5 \mu\text{m}$.

2.6.1.2 Sputtering

Bill et al.⁽⁵⁾ reported the sputter deposition of an Y_2O_3 stabilized ZrO_2 primer to the Ni-Cr-Al-Y bondcoat of a 403 SS substrate.

Sputter deposition of YSZ was performed using an argon ion beam source of diameter 10 cm with a plasma bridge neutralizer. The YSZ sputter target (30 cm in diameter) was located 15 cm from the ion source at an angle of 45° with respect to the beam. The substrate was parallel to the target and separated from it by 15 cm.

Deposition procedure was as follows:

- (1) The sputter target was ion cleaned for 2.5h at an ion energy of 1200 eV and an ion current density of 0.5 mA cm^{-2} . The pressure was 5×10^{-5} Torr.
- (2) The substrate was outgassed at 5×10^{-7} Torr for 45 min.
- (3) The target was ion cleaned for 5 min.
- (4) The substrate was ion cleaned for 5 min at 1200 eV and 0.5 mA cm^{-2} .
- (5) An air leak into the vacuum chamber was adjusted until the pressure reached 1×10^{-3} Torr. YSZ was sputter deposited at 1300 eV and 0.5 mA cm^{-2} for 18.5h to yield a YSZ film thickness of about $1.5 \mu\text{m}$. (The film is assumed to be YSZ).

The as-sputter-deposited YSZ film on a plasma-sprayed Ni-Cr-Al-Y substrate is shown in Fig 3.

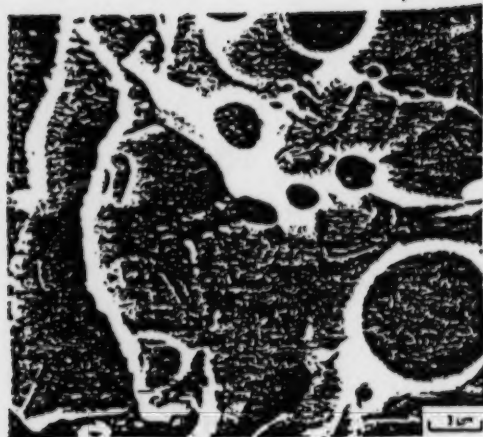


Fig.3 Sputter-deposited YSZ on a plasma-sprayed Ni-Cr-Al-Y bondcoat surface.

From Ref.3

Croset et al. (6) reported the deposition of calcia-stabilized zirconia thin films (500-17000 Å) on silicon substrates by rf sputtering.

The system was pumped down to 2×10^{-7} Torr before introducing the gases for the plasma discharge. The cathode was made by the sintering of a mixture of CaO and ZrO_2 powders. The plasma atmosphere was pure krypton, pure oxygen, or a mixture of the two gases, and the total pressure was stabilized at 5×10^{-3} Torr. All the deposits were made at a constant discharge power of 600W. The single-crystal silicon substrates were degenerately doped n type ($p \approx 10^{-3}$ Ωcm) and oriented (100). They were cleaned by successive treatments in acetone, hydrofluoric acid, and deionized water. This procedure limits the thickness of the surface oxide to less than 20 Å ($(5-10) \times 10^{15}$ oxygen atoms/cm²).

Pawlewicz and Hays (7) deposited ZrO_2 and ZrO_2 stabilized with CaO (30 mol%) or Y_2O_3 (10 mol%) on fused silica discs or nickel rods. Conditions during the sputtering experiment are listed in Table 1.

TABLE I
SPUTTER DEPOSITION CONDITIONS AND MICROSTRUCTURES OBTAINED FOR ZrO_2 COATINGS

Sputtering conditions ^a			Microstructure ^b		
Gas pressure (Pa)	[Ar]/[O ₂] (%)	Substrate bias (V)	Crystal structure	Grain size (nm)	Preferred orientation
2.7	90/10	≈ 0	Monoclinic ^c	≈ 100	(113 or 213)0.33
2.7	50/50	≈ 0	Monoclinic ^c	≈ 100	(113 or 213)0.4
13.3	90/10	≈ 0	Monoclinic	≈ 130	(200)0.7
	50/50	≈ 0		Glassy ^d	
8.0	70/30	-250	Monoclinic	≈ 100	(200)0.3, (113)0.6
2.7	90/10	-500	Monoclinic	30-100	(200)0.6
2.7	50/50	-500	Monoclinic	≈ 100	(200)0.9
13.3	90/10	-400	Monoclinic	30-100	(200)0.9
13.3	50/50	-400	Monoclinic	≈ 100	(200)0.9

^aTarget power density, 3 W cm⁻²; fused silica substrates; substrate temperature, 475 K.

^bX-ray diffractometer analysis.

^cSome small tetragonal peaks.

^dDeposition made twice with the same results.

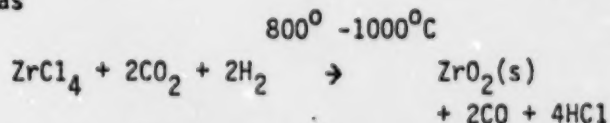
From Ref. 7

2.6.1.3 Chemical Vapor Deposition

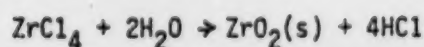
(a) Pyrolysis of Zirconium Compounds

Tauber et al. (8) reported ZrO_2 films in the thickness range of 500-8000 Å prepared by chemical vapor deposition in the temperature range of 800^o-1000^oC. The films were identified as fine-grained (≈325 Å), nearly stoichiometric, monoclinic ZrO_2 .

The reaction chosen to produce the ZrO_2 films is written in overall form as



which is conjectured to proceed in two steps



where H_2O is formed near the heated substrate.

The deposition apparatus is shown schematically in Fig. 4. The substrate rests on a molybdenum susceptor, which is heated inductively. The gases are carefully metered through Brooks rotometers and are transported through stainless steel lines to the 50 mm quartz reaction chamber. The ZrCl_4 is transferred to the chamber by passing hydrogen through a heated saturator. The carrier gas is forced to take a tortuous path over six layers of ZrCl_4 . All lines downstream from the saturator are heated approximately 20°C above the saturator temperature in order to prevent recondensation of the ZrCl_4 prior to its arriving at the heated substrate.

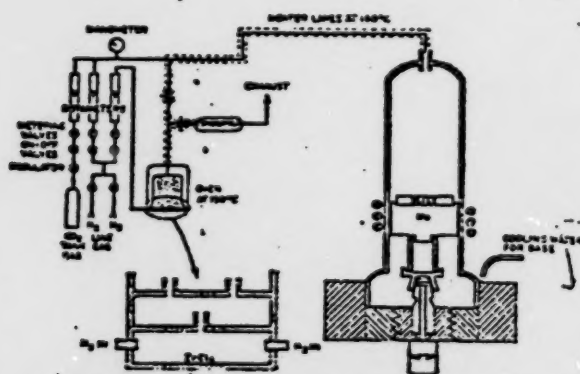
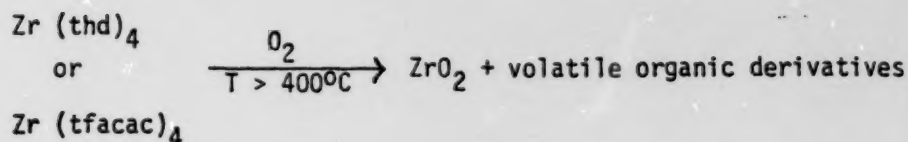


Fig. 4 Schematic representation of deposition equipment

From Ref. 8

Successful depositions were made with substrate temperatures between 800° and 1000°C on various substrates. Most often, the depositions were done at 900°C on 3-7 ohm-cm, (100), n-type silicon using the following concentrations of reactants: ZrCl_4 , 0.01%; CO_2 , 2.48%; the remainder hydrogen. Total hydrogen flow was ~ 3 l/min. Depositions were also made on 0.001 ohm-cm silicon, thermal SiO_2 , and fused silica disks.

Balog et al. ⁽⁹⁾ reported the deposition of ZrO_2 films on silicon substrates by oxygen-assisted decomposition of zirconium- β -diketonates at temperatures of 400 - 500°C . The CVD reaction can be summarized as:



The optimal deposition conditions are given in Table 2.

TABLE 2

THE OPTIMAL DEPOSITION CONDITIONS FOR ZrO_2 FILMS AT 400–500 °C WITH A MIXTURE OF H_2 (2500 ml min^{-1}) AND O_2 (1000 ml min^{-1})

Source material	Evaporation temperature (°C)	Flow rate of helium through the bubbler ^a ($\text{cm}^3 \text{min}^{-1}$)	Total flow rate ($\text{cm}^3 \text{min}^{-1}$)	Growth rate of the layer at 500 °C ($\text{\AA} \text{min}^{-1}$)
Zr(acac)_4	200	300	3800	60–70
Zr(thd)_4	210	400	3900	30–40
Zr(tfacac)_4	180	300	3800	120–130
Zr(Ifacac)_4	190	300	3800	170
Zr(hfacac)_4	65	100	3600	120

From Ref. 9

tfacac is trifluoroacetylacetonate

thd is tetramethylheptadionate

2.6.1.4 Spray Pyrolysis

Blandenet and coworkers⁽¹⁰⁾ reported the deposition of a ZrO_2 coating by the pyrosol technique. The coating was produced by spraying a solution of butyl orthozirconate in butanol or acetyl-acetone on glass or stainless steel.

2.6.1.5 Hydrolysis

Sviridova⁽¹¹⁾ reported the deposition of a ZrO_2 film on the surface of fused quartz by the hydrolysis of an alcoholic solution of zirconium tetrachloride and the diethyl ester of orthozirconic acid. The films underwent various thermal treatments, the baking temperature varying within the range of 120–180°C.

2.6.1.6 Reactive Evaporation

El-Shanshoury et al.⁽¹²⁾ reported the preparation of ZrO_2 films by evaporating zirconium in vacuum ($\sim 10^{-4}$ Torr). The affinity of zirconium for oxygen results in the formation of ZrO_2 during evaporation. A higher vacuum (10^{-6} Torr) is needed to obtain metallic films.

2.6.1.7 Doctor Blade Method

Yanagida et al.⁽¹³⁾ reported the deposition of dense, translucent ZrO_2 films (stabilized by Y_2O_3) by a modified doctor blade method. Loosely coagulated ceramic powders left after decomposition of methyl cellulose film were pressed onto polystyrene film to densify the powder compact. The films were heated at $1700^\circ C$ in air.

2.6.1.8 Anodization

Misch and Ruther⁽¹⁴⁾ reported the anodizing of zirconium in solutions of nitric acid. Hafnium-free zirconium was used in the preparations. Specimens were cleaned by wet grinding and polishing to 400 grit paper, followed by pickling. Platinum gauze was used as the cathode (potential + 1.10V vs. saturated calomel, polarized potential + 1.05V).

Mitchell and Salomon^(15,16) reported the production of anodic zirconium and oxide films. Zirconium foil 0.8 mil thick containing approximately 0.2% Hf. and other impurities was cleaned in an etch solution containing 50% distilled H_2O , 45% HNO_3 and 5% HF. The film was then washed to remove fluoride and anodized on one side at 100V for 18 hours in a sodium borate-boric acid, electrolyte buffered at pH9.

2.6.1.9 Low Temperature Oxidation

Balakir et al.⁽¹⁷⁾ reported a coating deposition method by low temperature oxidation of zirconium alloys in oxygen in the presence of fluoride catalysts. The optimal oxidation conditions are as follows:

$T = 350-450^{\circ}\text{C}$

oxidation rate : up to $1\text{ }\mu\text{m/min ZrO}_2$

Expenditure of fluoride catalyst 50g/litre of reaction volume.

The process is controlled by reducing the oxygen pressure.

2.6.2 Properties

2.6.2.1 Thermally Sprayed Coatings

Figure 5 shows the relation between growth rate and plasma current for the deposition of ZrO_2 , HfO_2 and ThO_2 plasmas reported by Kawabuchi and Magari (1).

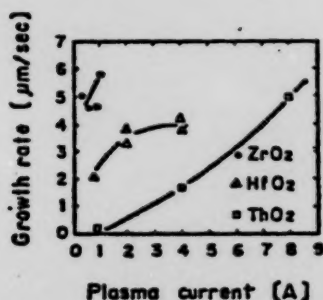


FIG. 5. The relation between the plasma current and growth rate for the deposition from ZrO_2 , HfO_2 , and ThO_2 plasmas.

From Ref. 1

Yields, given as ratios of deposition rate to evaporation rate attain values as high as 90% for ZrO_2 coatings. The deposition rate, growth rate, and the current efficiency increase with the plasma current and with feeding O_2 gas into the plasma. On the other hand, heating a cathode externally or feeding Ar gas into them leads to the reduction of those rates, the current efficiency and yield (90%). Mass-spectrometric analyses showed the main depositing ion species is ZrO^+ for the deposition from the ZrO_2 plasma. The deposits are monoclinic ZrO_2 with precipitates of metallic $\alpha\text{-Zr}$.

Nicoll and coworkers (2) reported the deposition of air sprayed Ni-Al-Cr-Y/ZrO₂-Y₂O₃. The coatings, described earlier in Section 2.6.1.1 had a thickness for the Ni-Cr-Al-Y layer between 100 and 150 μm and for the ZrO₂-Y₂O₃ layer between 200 and 300 μm . The coatings were intended for use in helium cooled high temperature reactors (HTRs) which primarily have to resist wear.

Samples of the coated species were found to have improved thermal shock resistance. Using a fluidized bed facility with bed temperatures of ambient and 950°C and air as the fluidizing bed medium it was reported that the coated samples withstood at least 300 cycles using a bed dwell time of 5 min. Spalling was not observed. The use of Ni-Al or Ni-Cr bond coats leads to spalling within 14 cycles.

Static loading test (80N.cm⁻² at 1050°C in HTR helium over 100 hours) showed that self-welding was absent. The dynamic sliding wear resistance was studied by moving the ceramic surfaces of a sample block and plate against each other under two combinations of temperature and stress, namely 850°C and 2000 N.cm⁻² and 950°C and 500 N.cm⁻². All tests were carried out in helium with sliding distances of 5 and 20 cm and velocities of 1mm.min⁻¹. The self-welding and friction tests set-up are shown in Figure 6.

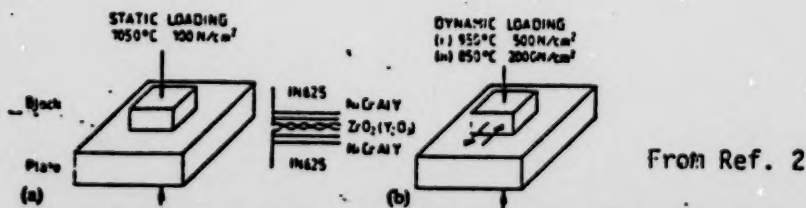
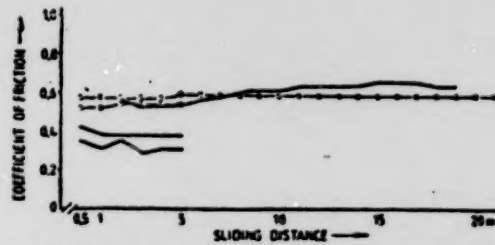


Fig. 6 Schematic diagram of (a) the non-self-welding tests and (b) the sliding wear tests in HTR helium.

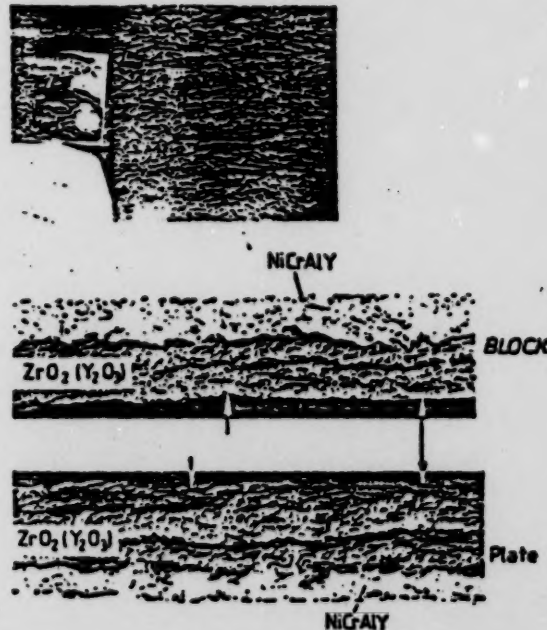
The coefficient of friction versus sliding distance is graphically represented in Figure 7.



From Ref. 2

Fig. 7 Coefficient of friction for ZrO_2 on ZrO_2 as a function of sliding distance: —, 850°C , 2000 N cm^{-2} ; ---, 950°C , 500 N cm^{-2} .

As can be seen the $950^\circ\text{C}/500 \text{ N cm}^{-2}$ regimen gives a lower coefficient of friction (0.3-0.4) than the $850^\circ\text{C}/2,000 \text{ N cm}^{-2}$ regimen.



From Ref. 2

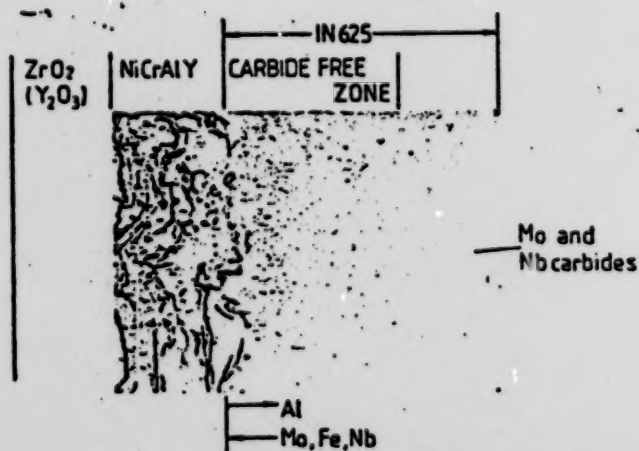
Fig. 8 Structures of the duplex coating after 5 m sliding distance at 950°C and 500 N cm^{-2} in HTR helium.

The coating on the block and plate after a sliding distance of 5 m at 950°C and a stress of 500 N cm^{-2} is shown in Figure 8. The macrograph shows that partial spalling has occurred on one area of the block, which

amounts to nearly 20% of the total. Scoring can be seen on the plate in the direction of the movement. This is shown more clearly in the metallographic sections. The surfaces of both the block and the plate exhibit scoring and smooth areas where the ceramic layer has been rubbed flat. In both cases the ceramic layer is cracked parallel to the Ni-Cr-Al-Y coating.

The corrosion resistance of the coatings was measured by exposure of the sprayed layers to HTR helium for 3000 hrs at 950°C. A hermetically sealed container is used to maintain the very low O_2 partial pressures required. X-ray diffraction after the test showed the ZrO_2 - Y_2O_3 layer to be unaffected by exposure. The material remained fully stabilized compared with the initial state.

Diffusion of helium through the ceramic layer, which is porous and cracked, can lead to carburization of the Ni-Cr-Al-Y layer. The formation of chromium carbides which are brittle could lead to coating degradation and spallation. In this test, spalling did not occur and the microstructure of the Ni-Cr-Al-Y layer on the IN 625 substrate is shown in Figure 9.



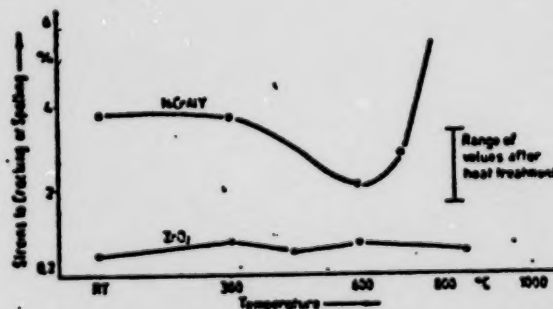
From Ref. 2

Fig. 9. Microstructure of the (Ni-Cr-Al-Y)-IN 625 interface after 3000 h exposure at 950°C in HTR helium.

Strains occur under service conditions because of thermal expansion mismatch or mechanical loading. Exceeding the limited ductility of a coating can lead to cracking and spallation.

Therefore, the coating has to exhibit a certain ductility in the as-sprayed state. This was measured here using strain tolerance tests at temperatures up to 850°C for both the Ni-Cr-Al-Y and the ceramic layers individually.

The substrate material used was not IN 625 but the properties of the base material are not expected to affect the results obtained. The results are shown in Figure 10. The values for $\text{ZrO}_2\text{-Y}_2\text{O}_3$ remain extremely low (less than 0.7%) at all test temperatures. In comparison, the Ni-Cr-Al-Y values lie between 2% and 4%. It could be demonstrated using a constant rate heat treatment cycle that the strain to cracking can be raised to between 1.7% and 3% at 850°C. This heat treatment can be performed in vacuum or air.



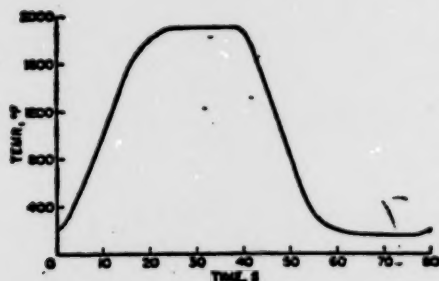
From Ref.2

Fig. 10. Strain to cracking as a function of temperature for the Ni-Cr-Al-Y and $\text{ZrO}_2\text{-Y}_2\text{O}_3$ layers.

Buckley (3) carried out a comparative study on the use of flame spraying and plasma-arc spraying for the deposition of zirconia coatings and zirconia-nickel-aluminide cermet coatings on Ni-Co-Mo metal. Coating thickness was found to be between 0.009 and 0.024 inch.

Thermal shock tests were made on the Ni-Mo-C alloy specimens which were coated with zirconia and the zirconia-nickel aluminide cermet to determine if coating thickness and/or method of application affected degree of spalling.

Figure 11 presents a typical thermal shock cycle. This curve was generated from total radiation pyrometer readings taken on the hot-coated surface of several typical specimens. It shows that temperature of coatings changed approximately 1700°F in 20 s when cycled between 200° and 1900°F.



From Ref. 3

Fig. 11 Typical cycle for the thermal shock and insulation tests (hot loss).

Table 3 shows the results of specimens subjected to thermal shock cycles. The flame-sprayed stabilized zirconia and the plasma-sprayed zirconia-nickel aluminide cermet were superior to the plasma-sprayed zirconia specimens. It was also noted that spalling of plasma-sprayed zirconia coating occurred regardless of coating thickness.

Fracture of the zirconia plasma-sprayed coating is believed to have resulted because of the relatively poor thermal shock resistance of zirconia compounded by the greater density characteristic of plasma-spray coatings as compared to flame-sprayed zirconia coatings. The good thermal shock resistance of the cermet spray coating is believed to result from the higher thermal conductivity of the nickel and aluminum components in the cermet spray composition.

Table 3 Coated Hastelloy-X Specimens Subjected to 50 Thermal-Shock Cycles or to Failure. Δt on Heating and Cooling was $\approx 1700^\circ\text{F}$ in 20s

Coating thickness (in.)	ZrO ₂ flame-spray	Testings tested ZrO ₂ plasma-spray	ZrO ₂ cermet plasma-spray
0.009	No failure	3 cycles	No failure
0.015	No failure	31 cycles	No failure
0.024	No failure	49 cycles	No failure

From Ref. 3

The coatings were also found to be very effective thermal insulating barriers on the basis of thermal conductivity values calculated from experimental data (see Table 4).

Table 4 Thermal Conductivity of Coated Specimens

	$K = \text{Btu}/(\text{ft}^2 \text{ hr } ^\circ\text{F})$
Hastelloy-X, uncoated	203.5
Hastelloy-X + cermet coating	30.3
Hastelloy-X + flame-sprayed ZrO ₂ coating ...	21.8

*Extrapolated, Ref. 11.

From Ref. 3

The conclusions of this investigation were:

1. Flame-sprayed zirconia coating has greater thermal shock resistance than plasma-sprayed zirconia coating of similar composition and coating thickness.
2. Flame-sprayed zirconia coating is a better thermal insulator than the plasma-sprayed cermet coating.
3. Insulation capacity of flame-sprayed zirconia coating on Ni-Mo-C alloy is a linear function of thickness between 0.006 and 0.024 in.

Zakharov and Trofimov ⁽⁴⁾ reported the deposition of zirconia on steel and glass substrates by flame spraying with an oxyacetylene torch.

It was found that the adhesion of the sprayed coatings depended to a large extent on the degree of particle fusing. The adhesion and thermal shock resistance of a deposit were found to increase with increasing size of

the heat exchange zone in the torch nozzle, with increasing arc power, and with decreasing distance from the substrate.

2.6.2.2 Sputtering

Bill et al.⁽⁵⁾ conducted cyclic thermal shock experiments on specimens simulating two different turbine seal candidate systems. The systems differed in the type of strain isolator intermediate layer employed between the plasma-sprayed YSZ layer and the substrate. In particular, the effect of the presence of a sputter-deposited YSZ layer applied to the Ni-Cr-Al-Y boncoat before deposition of the plasma-sprayed YSZ layer was assessed.

It was observed that application of sputtered YSZ primer improved the thermal shock life of a specimens with a sprayed porous Ni-Cr-Al-Y intermediate layer by a factor of 5-6. Significantly reduced laminar cracking was observed in the specimen with the primer.

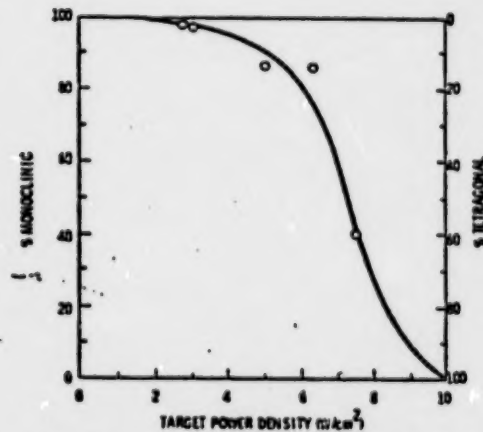
The authors concluded that the plasma-sprayed YSZ particles more effectively wet and adhere to the bondcoat when the YSZ primer is present. Also, the cooling and solidification rate of impinging molten plasma-sprayed YSZ particles is retarded when the primer is present, allowing for the formation of a more compact first layer of sprayed particles with a less detrimental stress distribution.

Croset et al.⁽⁶⁾ deposited calcia-stabilized zirconia thin films (500-17000 Å) on silicon substrated by rf sputtering. The deposits obtained were found to be stoichiometric and homogeneous if the plasma was pure oxygen or krypton containing at least 0.2% oxygen. Deposits were prepared with low porosity (>1 defect/min²). A CSZ thin film of the fcc fluorite-type structure was obtained at temperatures below 600°C.

Pawlewicz and Hays⁽⁷⁾ used r.f. diode reactive sputtering to deposit ZrO₂ coatings as well as mixed ZrO₂.CaO and ZrO₂.Y₂O₃ coatings on fused silica substrates. By correlating the results of microstructural observations with composition variations and target power density the authors

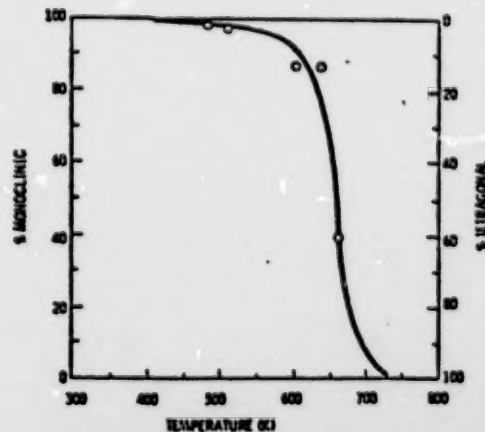
reached the following results.

Additions of Y_2O_3 and CaO to the sputtering target permit the deposition of cubic ZrO_2 coatings compared with the monoclinic coatings which are obtained from pure ZrO_2 targets. The target power density can be used to select any desired monoclinic-tetragonal phase composition for pure ZrO_2 through its influence on the substrate temperature. (Figures 12, 13 and 14).



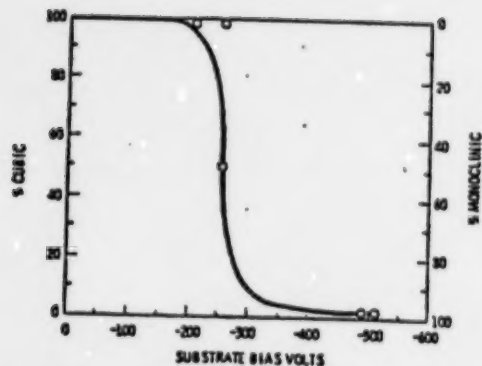
From Ref. 7

Fig.12 Dependence of crystalline phase composition on target power density for ZrO_2 coatings. The deposition conditions were 90%Ar-10% O_2 sputtering gas mixture, 2.7 Pa total gas pressure, zirconium target and d.c. floating substrate.



From Ref. 7

Fig.13 Estimated dependence of crystalline phase composition on substrate temperature for ZrO_2 coatings (same deposition conditions as Fig. 1).



From
Ref. 7

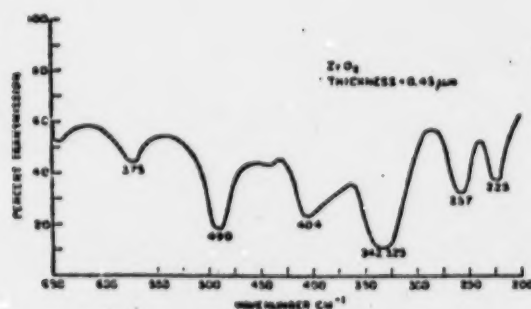
Fig. 14 Dependence of crystalline phase composition on substrate bias voltage for $\text{ZrO}_2\text{-CaO}$ coatings. The deposition conditions were 3 W cm^{-2} target power density, approximately 475 K substrate temperature and a $\text{ZrO}_2\text{-15mol\%CaO}$ target.

Substrate bias allows broad and potentially useful manipulation of both the grain size and the preferred orientation of monoclinic ZrO_2 and cubic $\text{ZrO}_2\text{-CaO}$. Substrate bias also permits control of the cubic-monoclinic phase composition of $\text{ZrO}_2\text{-CaO}$ by causing a preferential loss of calcium relative to zirconium in proportion to the bias voltage. The deposition rate appears to influence the grain size of $\text{ZrO}_2\text{-Y}_2\text{O}_3$ coatings. The oxygen partial pressure and total sputtering gas pressure have no observable influence within the range examined. The monoclinic-tetragonal transformation temperature appears to be near 650 K for sputtering as opposed to about 1273 K under equilibrium conditions.

2.6.2.3 Chemical Vapor Deposited Coatings

Tauber and coworkers ⁽⁸⁾ reported optical, chemical, electrical and interfacial properties of ZrO_2 films deposited on silicon substrates by chemical vapor deposition from ZrCl_4 , CO_2 and H_2 . Substrate temperatures between 800 and 1000°C were used. Identification of the films was carried out using electron microprobe analysis, infrared absorption and transmission electron microscopy. Electron microprobe analysis showed that the films had the following composition: Zr: $34.23 \pm 0.50\%$, O: $64.95 \pm 0.52\%$, Si: $0.81 \pm 0.02\%$ (atomic percentages).

The infrared spectrum of ZrO_2 on silicon is shown in Figure 15. The electron diffraction pattern obtained from transmission electron microscopy is listed in Table 5. The pattern matches closely that of monoclinic ZrO_2 . The films were found to be clear, hard, crystalline and adhesive. Films as thick as 8000 Å did not show signs of cracking.



From Ref. 8

Fig. 15 Infrared transmission spectrum for ZrO_2

Table 5 Indexing of ZrO_2 electron diffraction pattern

Ring number	Plane (hkl)	d(hkl) theoretical	I/I ₀ theoretical	d(hkl) calculated	Observed intensity
1	(100)	3.05	5	3.15	W
2	(011)	3.69	15	3.69	W
3	(111)	3.16	100	3.15	VS
4	(111)	2.84	65	2.82	S
5	(002), (020)	2.62, 2.60	20, 12	2.60	W
6	(021)	2.33	5	2.31	W
7	(211)	2.21	5	2.20	VW
8	(211)	1.900	7	1.99	W
9	(022)	1.846	15	1.83	W
10	(112)	1.802	12	1.80	W
11	(221)	1.761	5	1.77	W
12	(300), (202)	1.493	10	1.68	W

* W, weak; S, strong; VW, very weak; VS, very strong.

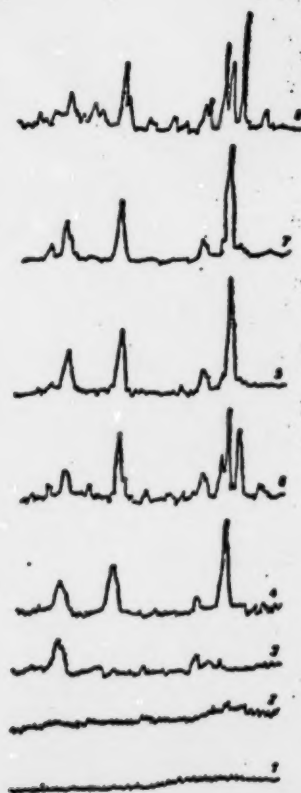
From Ref. 8

Balog et al.⁽⁹⁾ reported the use of CVD to deposit ZrO_2 films from zirconium β -diketonates in the 400-550°C range. The deposits, fine grained nearly stoichiometric monoclinic ZrO_2 , were hard and showed strong adherence to the substrate. The deposits were found to be comparable in quality with those prepared at 800-1000°C from ZrCl_4 , H_2 and CO_2 .

2.6.2.4 Hydrolysis

Sviridova ⁽¹¹⁾ reported the deposition of ZrO_2 films on fused quartz substrates by the hydrolysis of alcoholic solutions of $ZrCl_4$ and $ZrCl_2(OC_2H_5)_2$.

The thickness of the films varied between 0.1 and 1 μm . The X-ray diffraction patterns of the films and zirconium dioxide samples are shown in Figure 16. Table 7 lists the data on the optical properties, the state of aggregation, and the transmission limit of zirconium dioxide films.



From Ref. 9

Table 7 Changes in the Refractive Index, Thickness of the Film and the State of Aggregation of Zirconium Dioxide

Baking Temperature ($^{\circ}C$)	Refractive Index	Film Thickness ($\text{\AA}$)	Loss of water and solvent (%)	State of aggregation of sample and film	Transmission limit of ZrO_2 films for $\lambda = 6400 \text{ \AA}$
120	1.83	2000	27.5	Amorphous	280-290 m μ
200	1.90-1.92	1700	13.5	Amorphous	280-290 m μ
300	1.98-1.99	1500	3.0	Amorphous-crystalline	Transmission reduced by 10-7% in the region 290-320 m μ
400	2.02-2.03	900	1.0	Crystalline	Transmission reduced by 17-17% in the region 290-320 m μ
500	2.04	1380	0.94	Crystalline	
600	2.08	1360	0.50	Crystalline	

Fig. 16 X-ray "photographs" of films and zirconium dioxide samples as a function of baking temperature. Baking temperature (in $^{\circ}C$): curve 1-120; curve 2-200; curve 3-300; curve 4-400-500; curve 5-500-550; curve 6-600-650; curve 7-700-750; curve 8-800.

From Ref. 9

2.6.2.5 Reactive Evaporated Coatings

El-Shanshoury et al.⁽¹²⁾ reported the deposition of ZrO_2 films by reactive evaporation in vacuum ($\sim 10^{-4}$ Torr).

Evaporated thin films of ZrO_2 heated in air undergo the same sequence of polymorphic transformations as those annealed in vacuum. However, the temperatures at which the modifications exist are not the same. The intervals of stability of the modifications are as follows: (Figure 17)

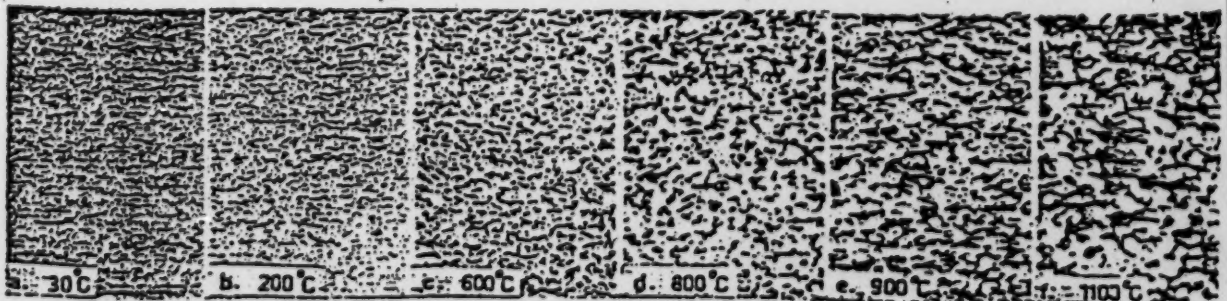
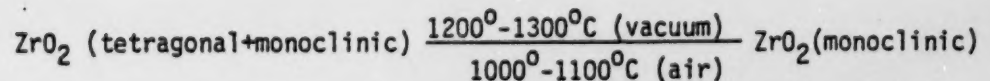
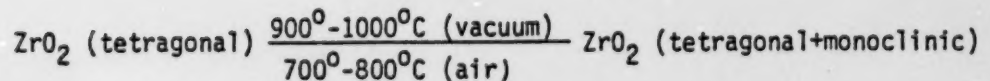
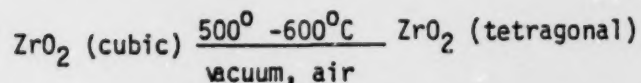
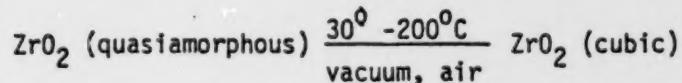


Fig 17 Transmission electron micrographs of air-annealed ZrO_2 from 30° to $1100^\circ C$ ($\times 13,000$).

The cubic/tetragonal transformation occurs at $600^\circ C$ in vacuum and in air. The replacement of the tetragonal by the monoclinic lattice starts at 800° to $900^\circ C$ during heating in air, about $150^\circ C$ lower than in vacuum. The

heterogeneous structure (tetragonal and monoclinic) exists between 800° and 1000°C. The monoclinic modification alone occurs when the film is heated above 1100°C. Figure 17 shows ZrO₂ films annealed in air between 30° and 1100°C. An average grain size of about 750 Å was estimated at 800°C (Fig. 17d). Figure 17e shows the nucleation of the monoclinic phase within the tetragonal grains.

2.6.2.6 Doctor Blade Method

Yanagida et al.⁽¹³⁾ reported the preparation of YSZ films using a modified doctor blade method. The thickness of the films obtained at 1700°C was ~100 µm. Grain size, density and translucency of the films were found to increase with increasing sintering temperature.

2.6.2.7 Anodization

Misch and Ruther⁽¹⁴⁾ reported the anodization of zirconium in solutions of nitric acid. At 1mA/cm² and concentrations of nitric acid exceeding 14 wt%, zirconium was found to develop a low-resistance oxide layer. As the concentration of nitric acid was increased, the anodic layer changed in appearance from white to gray to black. These products were all monoclinic ZrO₂.

Mitchell and Salomon^(15,16) reported the preparation of ZrO₂ films using anodizing with HNO₃. The permeability of these films by KNO₃ was measured. The results suggest that the coating surface contains a reproducible network of interstices which serves as path for permeation. The observed activation energy for permeation through the oxide is nearly four times greater than the activation energy of for the free diffusion of KCl in water.

2.6.2.8 Low Temperature Oxidation

Balakir et al.⁽¹⁷⁾ reported a novel method to produce ZrO₂ coatings by the low temperature oxidation of zirconia alloys in the presence of fluoride catalysts. The porosity of the coatings was found to be 30-40%, the open

porosity being 65-85% of the total. The filtration coefficient was relatively low ($5-7 \cdot 10^{-4} \text{ cm}^2 \cdot \text{s}^{-1}$). The pores are mainly non-isomeric, 15-20 μm in size, with preferential orientation parallel to the substrate. Some coatings over 150 μm thick, in regions most remote from the substrate cracks, 10-20 μm wide, are observed up to 200 μm long, oriented parallel to the substrate. The occurrence of the cracks was attributed to thermal stresses. ZrO_2 was in the stable monoclinic modification.

2.6.3 Applications

There are several important applications of zirconia coatings either in the pure ZrO_2 form or with admixtures. Perhaps most important are applications based on CaO and Y_2O_3 stabilized ZrO_2 coatings used to improve the abrasion resistance of high temperature components, for use in turbines or nuclear reactors. The films themselves tend to be permeable and porous and consequently do not offer protection against chemical attack of the substrate.

As metallic zirconium is a construction material in nuclear fuel rods, some specialized coating methods have evolved which essentially oxidize the surface of zirconium alloys to produce an abrasion resistant coating. However, the components cannot exceed a temperature of 1100°C since a phase transformation will occur with subsequent loss of the film.

Another application for ZrO_2 is the production of antireflection coatings and beam splitters. They are sufficiently transparent in the ultraviolet that they are of particular importance for the antireflection coating of quartz and fluoride ⁽¹³⁾.

The thermal spraying methods (plasma, flame, and detonation gun) are probably the most important economically, judging by the number of papers on the subject. The other techniques require batchwork treatment of the substrate.

The applications of the coatings investigated in this survey are listed in Table 8.

TABLE 8: Applications of ZrO_2 Coatings Prepared by Various Techniques

Technique	Coating	Application	Reference
Plasma-Arc Spraying	ZrO_2	nuclear energy, jet engines, MHD power generation.	1
"	Ni-Cr-Al-Y/ ZrO_2 - Y_2O_3	improve wear resistance in He-cooled high temperature reactors.	2
Flame Spraying	ZrO_2 (CaO-Stab.)	thermal barrier coatings in aerospace vehicles.	3
"	ZrO_2 (Stab.)	to improve erosion resistance.	4
Sputtering	ZrO_2 (Y_2O_3 -Stab.)	apply a primer between bondcoat and plasma-sprayed YSZ to reduce laminar cracking.	5
"	ZrO_2 (CaO-Stab.)	electronic insulators.	6
"	ZrO_2 (pure, CaO-, Y_2O_3 -stab.)	thermal, electrical insulation, reduced friction loss, increased wear or erosion resistance, protection from oxidation, sulfidation or corrosion.	7
CVD	ZrO_2	insulating thin films.	8
"	ZrO_2	MIS films.	9
Spray Pyrolysis	ZrO_2	-	10
Hydrolysis	ZrO_2	antireflection	11
Reactive Evaporation	ZrO_2	thin films.	12
Doctor Blade Method	ZrO_2 (Y_2O_3 -Stab.)	dense, translucent thin films.	13
Anodization	ZrO_2	-	14,15,16
Low Temperature Oxidation.	ZrO_2	coatings for small shapes.	17

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3. SPRAY PYROLYSIS

3.1 Introduction

Spray pyrolysis is a process whereby a solution of compounds (usually salts) containing the cation(s) and anion(s) of interest is sprayed onto a hot substrate where the solution components react to form a film or coating of the desired composition. The interesting feature is that the source material is not transported as a vapour but as a solution in droplets. This allows transport at room temperature. When the droplet reaches the heated substrate, the solvent evaporates and a pyrolytic chemical reaction occurs. This process has been used extensively to produce metal oxides from halides or other salts.

Spray pyrolysis is a special case of chemical vapour deposition (C.V.D.). Although the range of compounds which can be deposited by spray pyrolysis techniques is presumably smaller than for classical C.V.D. owing to the lower reaction temperature, this spraying method has several advantages from a practical point of view^(1,2).

- (i) The source material does not need to be heated.
- (ii) No early decomposition will occur until the aerosol is in the neighbourhood of the substrate.
- (iii) Deposition of mixed compounds in a well defined composition is achieved by adjusting the solution composition. No separation during the transport occurs.
- (iv) The use of organometallic compounds allows moderate reaction temperatures (from 300 to 500°C). Thus, a larger variety of substrates can be used.
- (v) Owing to its simplicity, the method is less limited in sample size. Large surfaces can be covered. Continuous coating operations can be set up⁽³⁾.
- (vi) The deposition rate is higher than for C.V.D. and the equipment cost is much lower.

3.2 Spray Pyrolysis Technology

3.2.1 Equipment

The equipment for chemical spray deposition is schematically represented in Figures 1 and 2.

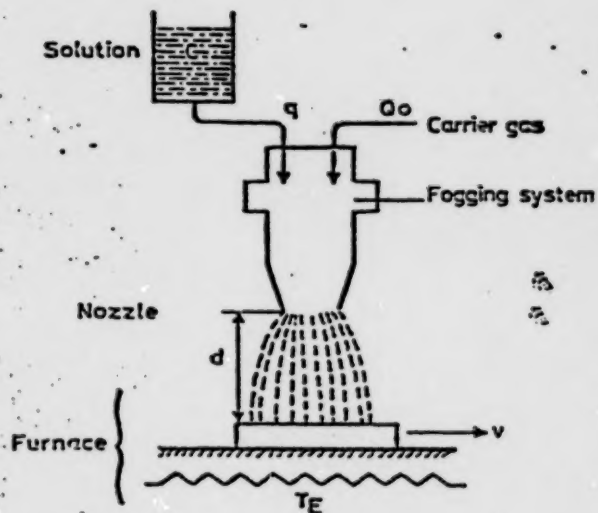


FIGURE 2: Schematic diagram of equipment for chemical spray Deposition (Ref. 4)

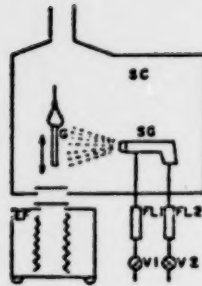


FIGURE 1: Schematic diagram of the spray-coating equipment. G, substrate glass; SC, spray chamber; SG, spray gun; FL1, flowmeter for solution; FL2, flowmeter for carrier gas; V1, needle valve to adjust the solution flow; V2, needle valve to adjust the carrier gas flow; EF, electric furnace. Ref. (12)

The substrate is heated in an electric furnace to a predetermined temperature. It is sprayed directly in the furnace (Figure 2) or after it was lifted from the furnace to the spray chamber (Figure 1). Spraying in the spray chamber is more feasible than in the furnace. But the variation and the rapid decrease of the substrate temperature in the spray chamber will become a negative factor^(4,12).

The equipment used to implement this process is simple and economical. The main components are a nozzle to spray the aerosol, (in some cases, an ultrasonic atomizer), a pyrolysis furnace and an exhaust system for the gases.

3.2.1.1 Spray Nozzle

The spray nozzle consists of a pipe having a diameter that is sufficiently large to avoid coalescence of the droplets. It directs the aerosol into the pyrolysis zone. The spray gun is usually constructed from stainless steel. This is not entirely satisfactory because corrosion may occur which will result in an oxide film containing iron⁽¹³⁾. A spray gun which is constructed from quartz has been used successfully⁽¹⁴⁾.

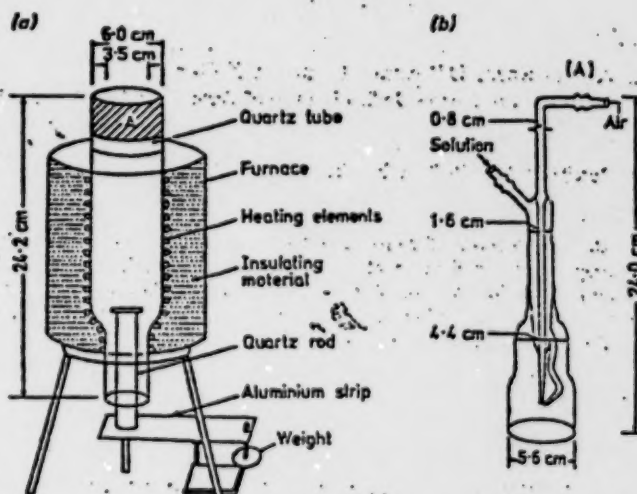


FIGURE 3: Set-up for spray deposition of In_2O_3 films
(Ref. 14)

The spray set-up is shown in Figure 3. Figure 3(a) gives the design of a special furnace used for spray deposition. A transparent quartz muffle 24.4 cm in length and 6 cm diameter at top and 3.5 cm at the bottom was used. The furnace is capable of giving 600°C at the position of the slide which is placed on the top of the quartz push rod. The quartz push rod can be placed in position by means of a weight and an aluminium strip.

Figure 3(b) gives the diagram of a sprayer which fits onto the top of the muffle at A. During the film preparation which is done under normal atmospheric conditions, an uncontrollable amount of oxygen is introduced into the film and acts as an electron trap. To eliminate this condition, all samples were annealed to about 300°C under high vacuum (10^{-5} Torr). The annealing process improves the quality of the coating.

3.2.1.2 Ultrasonic Atomizer

This comprises a glass vessel containing the liquid to be sprayed and filtered at the bottom with a ceramic transducer excited by a high frequency generator⁽⁵⁾.

Spray pyrolysis using ultrasonic atomization rather than the more conventional pneumatic atomization has been claimed to produce better quality coatings. Ultrasonic spraying produces droplets of a rather narrow size distribution. The aerosol produced by this method is, therefore, much more uniform and a better control over the coating parameters is achieved. An example of the improvement in droplet size distribution obtained with this technique is shown in Figure 5. Also, for ultrasonic spraying, the gas flowrate and the aerosol flowrate are independent. A lower gas flowrate can thus be used to prevent excessive cooling of the substrate.

3.2.1.3 Pyrolysis Furnace

The pyrolysis furnace may be cylindrical (Figure 4) or linear (Figures 2 and 3) in shape. Its primary role is to effect the heating of the glass substrates to the deposition temperature and then to promote vaporization of the solution

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FIG. 4. Comparative size spectra of atomized droplets: (a) pneumatic generation; (b) ultrasonic generation.

corresponding to the regional coating. Spraying can be done inside or outside the furnace.

3.2.1.4 Exhaust System

This is a depressurizing system that must satisfy two aims:

- (1) It must evacuate the effluent gases outside for safety reasons because the chemicals used may be toxic.
- (2) It must ensure that the gas mixture circulates near the substrates to be coated.

3.2.2 Chemistry

The conditions required for the deposition of a number of oxide films using the spray pyrolysis technique have been described by G. Blandenet⁽⁵⁾. These conditions are listed in Table 1.

TABLE 1

Conditions For the Deposition of Oxides by the Pyrosol Process

Coating	Source material	T_f^* (°C)	T_b^* (°C)	Solvent	Carrier gas	Reaction temperature (°C)	Type of substrate studied
Fe_2O_3	Iron acetyl-acetonate	181	200	Butanol	Air	300-500	Glass, stainless steel
Cr_2O_3	Chromium acetyl-acetonate				Air	520-560	Glass, In_2O_3 -coated glass
Al_2O_3	Aluminium isopropoxide	248		Butanol	Air	650	Glass
In_2O_3	Indium acetyl-acetonate	260	280	Acetyl-acetone	Air	480	Glass, alumina, silica (plates and fabric)
Y_2O_3	Yttrium acetyl-acetonate	190		Butanol	Air	600	Glass
V_2O_5	Vanadium acetyl-acetonate				Air	300-360	Glass
VO_2	Vanadyl acetyl-acetonate (AA) ₂ OV	180	200	Butanol	Air	360	Glass
SnO_2	Anhydrous stannic chloride			Methanol	Nitrogen, air	300-500	Glass, alumina
TiO_2	Butyl orthotitanate			Acetyl-acetone, butanol	Air, nitrogen	400	Glass, stainless steel
ZrO_2	Butyl ortho-zirconate			Butanol, acetyl-acetone	Air		Glass, stainless steel

(Ref. 5)

* T_f is the melting point and T_b the boiling point.

It can be seen that glass is the most widely used substrate material although metallic substrates & stainless steel have been used as well.

3.2.2.1 Reagents

The reagent must satisfy a number of essential conditions:

- (i) It should be stable at room temperature.
- (ii) It should not oxidize in air or in the presence of water vapor.
- (iii) It should have a decomposition temperature below 500°C and preferably higher than its boiling or sublimation temperature.

Generally the reagents employed are organometallic compounds (acetylacetonates, metal alkoxides, etc.) but sometimes mineral salts (fluorides, chlorides, etc.) are used.

3.2.2.2 Solvents

The selection of solvent is governed by the solute chosen. Commonly used solvents are acetylacetone and methanol because of their high volatility and low surface tension (11).

3.2.2.3 Solution Parameters

The concentration of the solution should be greater than 0.02 mg.L⁻¹. A concentration less than 0.02mg.L⁻¹ gives a rate of deposition which is too low for a feasible coating process. The upper limit of the concentration of the solution is limited to the solubility of the solute in the solvent. The

viscosity of the solution must also permit a high aerosol flowrate. The gelatinous phase due to hydrolysis of the aqueous solution, is undesirable because not only does the phase make spraying difficult, but it will not produce a film by condensation from the vapor. The formation of the gelatinous precipitate can be prevented by maintaining a low pH in the spray solution.

The solution quality can affect the composition and structure as well as the uniformity of the film. The mode of dissolution is important since different modes can cause precipitation or the formation of undesirable complex ions. The aging of a solution may also cause changes in the chemistry. Concentration of solutes will affect the rate of film formation, and the ratio of different solutes will control film composition. The ratio of precursor ions in solution will not necessarily be the same as that for the film. The nature of the solute will not only determine the ion form (e.g. complex, cluster or single ion) in the solution which controls film microstructure, but will also determine by-products of the reaction. These by-products should be readily removed in the fume duct before they can damage the film. The film composition will depend on both the reaction heats and reaction kinetics.

3.2.2.4 Carrier Gases

The carrier gas is chosen for its suitability in relation to the chemical reaction taking place. It should not react with solute or solvent in the vapor phase. For deposition of oxides, air is generally used. For deposition of metals, a protective atmosphere of nitrogen and hydrogen is recommended. Adherent layers of both metals and oxides can be obtained by chemical spray deposition. As shown in Table II, the only metals that can be prepared are the precious metals that do not form oxides. A typical carrier gas flow rate is $3-6 \text{ L.min}^{-1}$. (4)

TABLE II
Chemical Conditions of Deposition
(Ref. 4)

Layer	Starting compound	Solvent	Temperature T _a , °C	Carrier gas
FeO ₃	(AA) ₃ Fe	Butanol	400-550	Air
SnO ₂	BaCl ₂	H ₂ O + HCl	480-500	Air
In ₂ O ₃	(AA) ₃ In	Acetylacetone	470-520	Air
Cr ₂ O ₃	(AA) ₃ Cr	Butanol	520-580	Argon
V ₂ O ₅	(AA) ₃ V	Butanol	450-510	Oxygen
Pd	(AA) ₂ Pd	Butanol	300-350	N ₂ + H ₂
Ru	(AA) ₃ Ru	Butanol	380-400	N ₂ + H ₂

AA = acetylacetonate.

3.2.2.5 Vapor Phase Chemistry

Viquié and Spitz⁽⁴⁾ pioneered the spray pyrolysis technique for the deposition of metals and oxides on glass. Figure 1 gives a schematic of the deposition process. It can be seen that the temperature of the deposition process is critical.

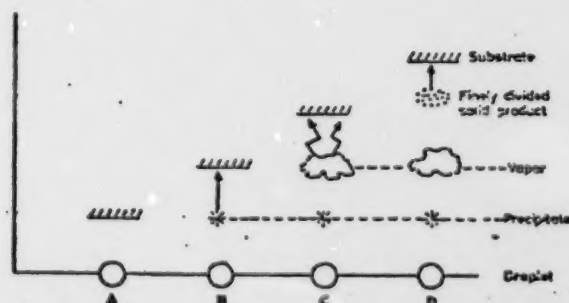


FIGURE 5: Description of the deposition process initiated With increasing substrate temperature. (Ref. 4)

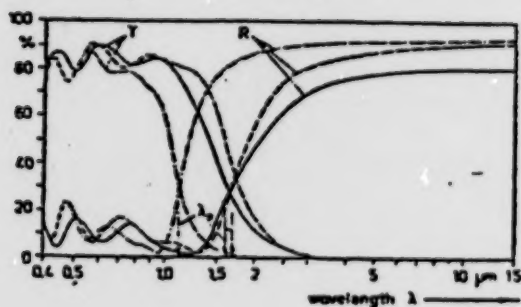


FIGURE 6: Spectral transmission T and reflection R of differently doped SnO_2 and In_2O_3 films on glass. λ_0 designates the plasma wavelength and the film thickness is $0.3 \mu\text{m}$.
 $\text{SnO}_2:\text{Sb}, N = 6 \times 10^{20} \text{ cm}^{-3}$, - $\text{In}_2\text{O}_3:\text{Sn}, N = 5 \times 10^{20} \text{ cm}^{-3}$.
 - $\text{In}_2\text{O}_3:\text{Sn}, N = 13 \times 10^{20} \text{ cm}^{-3}$ (Ref. 9)

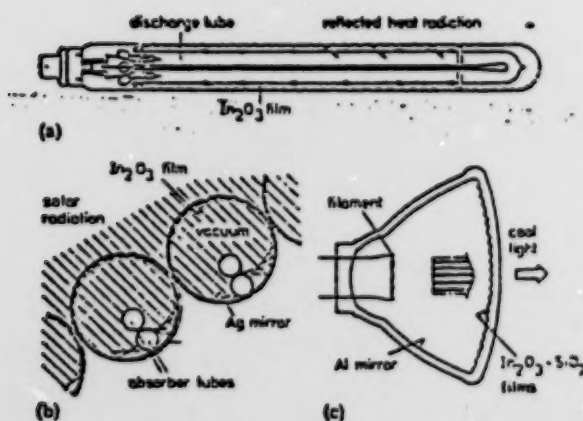


FIGURE 7: Three examples of applications of In_2O_3 films (a) sodium low pressure gas discharge lamp, (b) solar collector, (c) incandescent lamp with reflector (Ref. 9)

oxide coatings are also used in oven windows for heat reflection and in glass containers to improve their abrasion resistance.

3.3.2 CdS, Cu₂S

CdS/Cu₂S heterojunction cells look particularly promising in the field of photovoltaic research for the conversion of solar energy into electrical energy. This complex structure consists of active and passive elements. For a backwall cell, one of the passive elements is a conductive and transparent electrode (11).

The photoconductive films required for this application (thickness $\sim 1 \mu\text{m}$) are made of CdS, Cd(S,Se) and CdSe. Other applications for these materials are photoluminescent and cathode luminescent thin films with high resolution ($> 3,000$ line/pairs in) for solar cells. By spraying two $0.1 \mu\text{m}$ films, one of CuS and CdS on top of one another, cells with efficiencies of 4% have been produced. A typical example is shown in Figure 8.

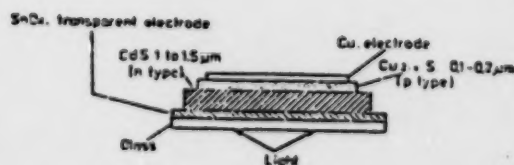


FIGURE 8: Schematic Diagram of a CdS/CuS cell.

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4. CHEMISTRY OF TIN COMPOUNDS FOR SPRAY PYROLYSIS

4.1 Introduction

Hydrolysis of the chloride has been the conventional method of SnO_2 film preparation. Starting reagents and procedures have been described for films of pure and doped SnO_2 (1-30). The properties of the films depend to a large extent on the conditions of the preparations, such as control of humidity (31), ion depletion to avoid alkali diffusion (32-34), precoating with SiO_2 (35,36), or by selectively etching alkali ions (37).

Apart from hydrolysis SnO_2 films have also been prepared by chemical vapor deposition (CVD) (38-40), spray pyrolysis (41-47), reactive sputtering of metal targets (48-52), rf sputtering of oxide targets (53-56) and by glow discharge (57,58).

Broadly speaking the compounds that have been used successfully for spray pyrolysis are the stannic salts, in particular the stannic halides, the dialkyltin carboxylates and tin alkoxides. This review will deal therefore mainly with the chemistry of tin compounds belonging to these classes.

4.2 Inorganic Tin Compounds

Tin occurs in two common oxidation states, +4 and +2. Of these, the +4 state is the more stable and consequently the chemistry of tin (iv) compounds is the more extensive and tin (iv) compounds are the more useful for spray pyrolysis.

4.2.1 Tin (IV) Halides

Representatives of this class of compounds have been used extensively for spray pyrolysis. The compound used most frequently is SnCl_4 which reacts with H_2O according to



This reaction which normally proceeds very rapidly can be modified by mixing the tin halide with ethanol, acetic acid or a mixture of both. The reaction proceeds slowly at 500°C and proceeds rapidly at 800°C. The breakdown of the organic constituents of the spray introduces reducing conditions and the resulting layer is of non-stoichiometric composition. At a temperature of 1000°C a layer of metallic tin is produced.

Of the four known tin (iv) halides SnF_4 is a hygroscopic crystalline white solid which sublimates at 700°C. Gaseous SnF_4 occurs most likely in the form of tetrahedral molecules but in the solid state SnF_4 differs from the other tin (iv) halides in that each tin atom is six-coordinate (59).

The physical properties of the other tin (iv) halides are shown in Table 2 and 3. It can be seen that the melting and boiling points increase with increasing atomic mass of the halogen atom. All three of the tetrahalides are volatile molecular species, in which discrete SnX_4 molecules are present in the gas, liquid and solid phases.

Tin (iv) chloride forms a number of hydrates. The hydrate which is stable at room temperature and 1 atm is $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$.

TABLE 1

PROPERTIES OF Sn(IV) CHLORIDE, BROMIDE AND IODIDE

Property	SnCl_4	SnBr_4	SnI_4
Colour	Colourless	Colourless	Brown
Melting point, °C	-33.3	31	144
Boiling point, °C	114	205	348
$\Delta H(\text{fusion})$, kcal/mole	2.19	3.15	4.53
$\Delta H(\text{vap})$, kcal/mole	7.96	10.39	13.61
Density, g/ml	2.23 (20°C)	3.34 (35°C)	4.56 (20°C)
Sn-X bond length (Å)	2.31	2.44	2.64
Vapour pressure ($\log_{10}$) (T in °Kelvin)	$7.59676 - \frac{1824.9}{T}$	$7.63048 - \frac{2270.8}{T}$	$7.66607 - \frac{2973.9}{T}$
Critical temperature, °C	319		
Critical pressure, mmHg	28,080		
Specific heat, cal/deg/g	0.1476		
Dielectric constant	3.2		
Magnetic susceptibility (per mole $\times 10^{-6}$)	-115	-149	

From Ref. 59

Tin (iv) chloride is soluble in aliphatic and aromatic hydrocarbons, carbon tetrachloride, and many other organic solvents.

TABLE 2

The Preparations and Properties of the Tin Tetrahalides

	SnF ₄	SnCl ₄	SnBr ₄	SnI ₄
Appearance	Colourless, hygroscopic solid	Colourless, volatile fuming liquid	White fuming crystalline solid	Yellow solid
m.p. °C		-33	30	143.5
b.p. °C	Sublimes at 705	114.1	293	343
Density	4.78	2.234	3.340	4.696
Solubility	Very soluble and is hydrolysed	Is hydrolysed		Is rapidly hydrolysed
Hydrates		SnCl ₄ ·5H ₂ O	SnBr ₄ ·4H ₂ O	
Preparation	Treat SnCl ₄ with HF	Treat tin with Cl ₂ in the cold	Treat tin with Br ₂	Treat tin with I ₂

From Ref. 60

Tin (iv) chloride forms a series of stannates, M₂SnCl₆. The hexahydrate of H₂SnCl₆ is claimed to decompose to HCl, H₂O and SnCl₄·5H₂O.

Tin (iv) bromide, SnBr₄, is a crystalline slightly hygroscopic substance. It is very stable thermally and can be purified by distillation. It decomposes under the influence of water.

Tin (iv) iodide, SnI₄, forms yellow to reddish crystals that decompose in water.

4.2.2 Tin (II) Halides

Bartholomew and Garfinkel (40) produced films of SnO₂ on 96% silica glass substrates by oxidizing anhydrous SnCl₂ with O₂ in air. The deposition reaction



has a free energy of -88 Kcal.mol⁻¹ at 700 K.

In process A, Figure 1, the droplet splashes on the substrate, vaporizes, and leaves a dry precipitate in which decomposition occurs.

In process B, the solvent evaporates before the droplet reaches the surface and the precipitate impinges upon the surface where decomposition occurs.

In process C, the solvent vaporizes as the droplet approaches the substrate, then the solid melts and vaporizes (or sublimates) and the vapor diffuses to the substrate to undergo a heterogeneous reaction there. This is true CVD.

In process D, at the highest temperatures, the compound vaporizes before it reaches the substrate and the chemical reaction takes place in the vapor phase.

Processes A and D lead to rough or nonadherent layers and are therefore of little interest.

3.2.2.6 Substrate Parameters

(i) Type of Substrate

The choice of substrate must satisfy a number of essential conditions:

- a) It should have a melting point higher than the spraying temperature. It should not soften or weaken at the spray temperature.
- b) It should be inert and should not disintegrate during heating to the spraying temperature.

- c) It should have a high enough heat capacity and temperature to heat the atomized spray into the vapour phase, heat the vapor to the reaction temperature while at the same time being subjected to radiative and convective heat loss.
- d) It should have a thermal expansion coefficient which matches the thermal expansion coefficient of the coating.
- e) The substrate should be chemically compatible with the coating. Oxide coatings are more compatible with oxide substrates (e.g. glasses or ceramics) than with metallic substrates.

(ii) Substrate Treatment

Various substrate surface treatments can improve the coating adhesion to the substrate body. B.J. Baliga⁽¹⁶⁾ reported substrate (glass or silicon) treatment which includes:

- a) degreasing in a 1:1:1 solution of isopropyl alcohol, trichloroethylene and acetone
- b) cleaning in Caro's etch [1:1 solution of H_2SO_4 (972) and H_2O_2 (472)].
- c) final rinsing in methanol

(iii) Temperature

The substrate in the spraying compartment is originally at the temperature to which it was heated, but will cool to some extent during the spraying operation. The amount of cooling will depend on the thickness and specific heat of the substrate, the spray time and the spraying conditions. A hard spray will have a greater surface cooling effect than a soft spray since more cooling air is introduced. Exothermic reactions will have a heating effect on the substrate surface. In order to produce temperature reproducibility, the original temperature of the substrate, time interval before spraying, spraying sequence and spray speed must all be reproducibly controlled. The substrate temperature can affect the composition of the film, its microstructure and adherence (4,13).

3.2.2.7 Coating Parameters

It was found that the different processes in chemical spray deposition depended not only on temperature but that the coating morphology is also influenced by the flow of the carrier gas, the substrate-nozzle distance, the droplet radius, solution concentration and solution flow rate^(5,6). These observations were found to be important for choosing conditions for the preparation of semitransparent photomarks. Typical values of the parameters for a pneumatic and a piezoelectric generator (ultrasonic atomizer) are shown in Table III.

TABLE III
Parameters of Chemical Spray Deposition
(Ref. 4)

Solution flow	Symbol	Piezoelectric transducer	Pneumatic transducer	Units
Temperature of the gaseous environment	T _a	400-550	500-550	°C
Flow of carrier gas	Q _c	3-6	3-6	liter/min
Distance between nozzle and substrate	d	3-15	40	mm
Droplet radius	r	1-4	5-30	microns
Solution concentration	C	0.1-0.4	0.1-0.4	moles/liter
Solution flow	q	30-60	500-800	cm ³ /hr
Speed of substrate through the furnace	v	10-40	10-40	mm/min

For spraying, the atomization air affects the cooling of the substrates, removal of fumes and the liquid flow, and all these parameters influence the film composition. The siphon height controls the liquid flow since it is affected by the density of the liquid. The spray pattern and distance of the substrate from the spray head will determine the uniformity of the coating. The spray sequence is also an important parameter.

For example, if a total spraying time of five seconds is required, often a sequence such as 1 sec. on, 1 sec. off five times gives superior quality film than a one-shot five second spray.

3.3 Coatings Produced by Spray Pyrolysis

The spray pyrolysis deposition method is very desirable since it lends itself readily to pilot and production scale work. Most coatings produced by spray pyrolysis are deposited onto glass substrates, with a few onto alumina, silica, chromium oxide and stainless steel. Coatings produced by spray pyrolysis have thicknesses that are usually less than one micron. Applications of transparent conductive coatings are in the fields of optics, electronics and solar energy utilization. The following types of coatings have been prepared:

3.3.1 In_2O_3 , SnO_2 , ITO Coatings

Thin films of doped indium oxide (In_2O_3), tin (IV) oxide (SnO_2), as well as mixed In_2O_3 - SnO_2 (ITO) coatings can be produced by spray pyrolysis. These films are transparent in the visible and near-infrared regions of the spectrum while they reflect radiation in the infrared region.

The coatings have high chemical and mechanical durability and adhere well to various substrates. Potential applications are numerous, particularly coatings for heat mirror systems as well as in solar cell technology⁽¹⁰⁾. Their spectral transmission curves are shown in Figure 6⁽⁹⁾. Three examples of applications of In_2O_3 films are shown in Figure 7. Other applications of In_2O_3 and SnO_2 coatings are in digital display systems (electrolytic, liquid crystals or light emitting screens) and films for antifrost and antimist optical devices. Tin (IV)

3.3.3 Other Metal Oxides

(i) ZnO

The requirements for a window material for a photo-voltaic heterojunction suitable for solar energy conversion is that it has a bandgap large enough to be transparent to most of the useful region of the solar spectrum, and that it has a resistivity small enough to prevent series resistance effects. Zinc oxide appears to be an n-type semiconductor that meets these requirements; its bandgap is 3.3 eV and its conductivity can be controlled over several orders of magnitude. The constituent elements are abundant and the material lends itself to a variety of thin-film deposition techniques including sputtering, vacuum evaporation, vapor transport and spray pyrolysis⁽¹⁷⁾. These properties, along with its non-toxicity and inherent low cost, make ZnO particularly attractive as a component of terrestrial solar cells. Exploratory investigations on n-ZnO/p-CdTe heterojunction solar cells prepared by sputtering and spray pyrolysis have been recently reported with short-circuit current values of 19mA/cm² and solar efficiencies of 4.6%.

(ii) Fe₂O₃, Cr₂O₃

It has been suggested that the spray pyrolysis technique could be used to produce thin films, Cr₂O₃ and Fe₂O₃ for decorative purposes⁽⁵⁾. However, no experimental work has been reported.

3.3.4 Miscellaneous Coatings

Noble Metals: Blandenet and coworkers reported that platinum, palladium and ruthenium have been deposited in the form of coatings used as catalysts for purifying engine exhaust fumes. When deposited on stainless steel previously coated with chromium oxide, they prove to be efficient catalysts extremely resistant to thermal shocks⁽⁵⁾. No experimental details were given by the authors.

Tin (II) chloride is commercially available as the dihydrate. One molecule of water is lattice equation while the other is coordinated directly to Sn ⁽⁶¹⁾. Anhydrous SnCl_2 can be obtained from the hydrated species by dehydration with acetic anhydride. In the solid state SnCl_2 may be considered to be nine-coordinate. In the gasphase SnCl_2 exists as discrete angular molecular species (see Figure 3).

SnBr_2 and SnI_2 have a polymeric layer structure in the solid state while forming discrete molecular species in the gasphase ⁽⁶²⁾.

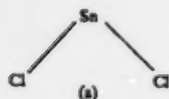
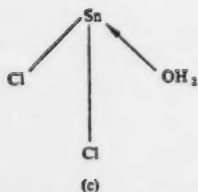
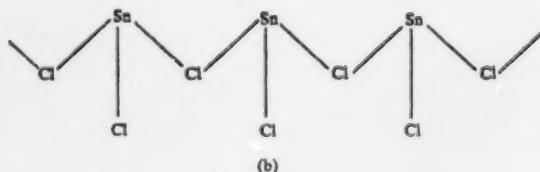


Figure 3



From Ref. 59

FIG. 17. Tin(II) chloride: (a) an angular discrete molecule in the gas phase; (b) the polymeric $(\text{SnCl}_2)_n$ chain present in crystalline SnCl_2 ; (c) coordination about tin in $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, where only one water molecule is actually coordinated to tin.

The SnCl_2 is normally dissolved in an ester, such as n-propyl acetate or an alcohol (e.g. glycerol, which evaporates on a heated substrate. The SnCl_2 is then oxidized with atmospheric oxygen to form the SnO_2 coating ⁽⁴⁷⁾.

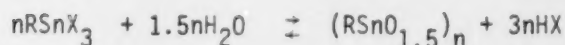
4.3 Organotin Compounds

4.3.1 Organotin Halides

Organotin chemistry is an extensive field based almost entirely on the use of these compounds as precursors ⁽⁶³⁾. The three basic types of organotin halides are R_3SnX , R_2SnX_2 and $RSnX_3$. Organotin halides have been used for the deposition of SnO_2 coatings ^(64,65).

Water and aliphatic alcohols have generally little effect on the symmetrical, saturated compounds. The Sn-C bond is generally more reactive in unsaturated organotins.

Organotin halides with small alkyl groups are soluble in water and aqueous acids. Hydrolysis is rapid and reversible. Some of the reactions are:



The organotins can be sprayed in pure form. The humidity of the air will provide water for hydrolysis and subsequent oxidation with removal of the alkyl groups leads to the formation of the SnO_2 film.

4.3.2 Organotin Carboxylates

Diorganotin carboxylates, $R_2Sn(OOCR')_2$, have been used as precursors for SnO_2 coatings ⁽⁴⁸⁾. R and R' are alkyl groups. R may preferably contain from 1 to about 8 carbon atoms, while R' preferably has from 1 to about 18 carbon atoms. Examples are dibutyltin diacetate, dipropyltin diacetate, dioctyltin diacetate, etc. ⁽⁴⁸⁾.

which is obtained as tetragonal crystals from aqueous AlF_3 at 100°C . When heated, it loses some 70% of its water at 200°C and most of the remainder at 700°C , though some loss of HF (and formation of Al_2O_3) also occurs, particularly if the hydrate is heated rapidly above 300°C .

b) Aluminum Chloride Hydrates $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$

Hydrated aluminum chloride dissolves readily in water, its solution has an acid reaction but contains no free acid. It is also soluble in alcohol.

The decomposition of aluminum chloride hexahydrate was examined by differential thermal analysis (D.T.A.) and thermogravimetry (T.G.) in combination with evolved gas analysis (D.T.G.). It was found that in the course of the decomposition reaction, the compound transformed into aluminum oxide through the formation of basic aluminum chloride as intermediate.^{(4) (5)} (Figures 1, 2 & 3)

Hydrated aluminum chlorides are used in deodorants, antiperspirants and fungicidal preparations in the formula $\text{Al}_2(\text{OH})_{6-n}\text{Cl}$ ($n=1-5$). These solutions must be buffered for the protection of skin and clothing because of their acidity. Aluminum chloride is also applied to difficult water treatment problems because of the excellent flocculence of aluminum hydroxide. Aluminum chloride is also used in roofing to improve adhesion of the asphalt containing Na_2SiO_3 .

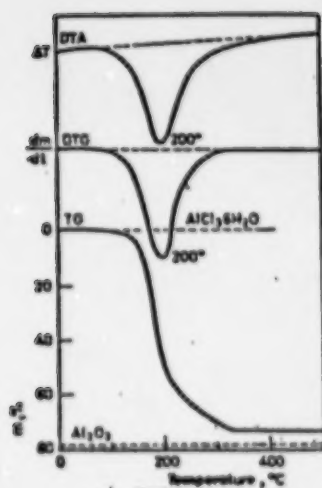


Figure 1: TG, DTG and DTA-Curves of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$
(Heating rate $5^\circ/\text{min.}$, Probe mass 241 mg,
 N_2 = atmosphere)

(Ref. 4)

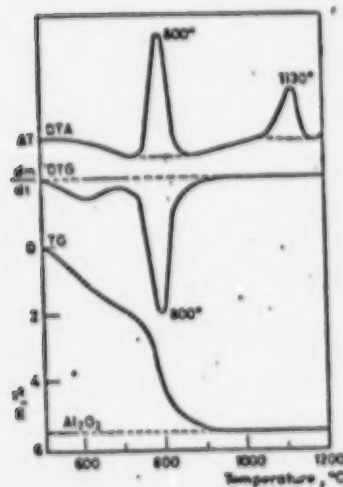


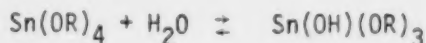
Figure 2: TG, DTG and DTA-Curve of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ above 500°
(Heating rate $7.5^\circ/\text{min.}$, Probe mass 197 mg,
 N_2 = atmosphere)

(Ref. 4)

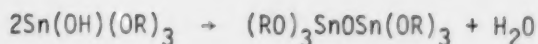
$R_xSn(OOCR')_y$ and $R_2Sn(OOCR')O(OOCR')SnR_2$ where R is an aliphatic or aromatic group and R' is a fluorocarbon of the structure C_nF_{2n+1} , (X=0-3, y=1 or 2, n is an integral number). Substrate temperatures range from 400 to 700°C. Solutions contain from 2 to 70% of the organotinfluoroacetic acid while 30 to 98% of methyl ethyl ketone, an organic solvent is present.

4.3.3 Tin Alkoxides

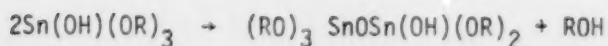
SnO_2 coatings can also be produced by hydrolysis, followed by polymerization of tin alkoxides. A final heat treatment step is required to remove entrapped water and organic residues. The hydrolysis step involves the replacement of an alkoxy by a hydroxy group



The polymerization step involves the condensation of the product of the above reaction



or



This sequence of reactions is the basis of the well known sol-gel process for the preparation of oxide glasses and ceramics at low temperatures.

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TABLE 2

PROPERTIES OF CRYSTALLINE ALUMINUM TRIHALIDES AlX_3

(Ref. 1)

	F	Cl	Br	I
Melting point (°C)	—	192.4	97.8	189.4
Sublimation temperature (1 atm; °C)	1272	180	256 ^a	381-2 ^a
$\Delta H_{\text{sublim.}}$ (kcal/mole)	71.5 ^a	28.0 ^a	8.6 ^a	26.8 ^a
ΔH_{fusion} (kcal/mole)	—	8.4	2.7	3.8
$-\Delta H_f^{\circ}$ (25°C; kcal/mole)	358	169	126	74
$-\Delta G_f^{\circ}$ (25°C; kcal/mole)	339	151	121	60
S° (25°C; cal deg ⁻¹ mole ⁻¹)	16	26	43	45
C_p (25°C; cal deg ⁻¹ mole ⁻¹)	18.0	22.0	24.0	23.6
Molecular weight	83.98	133.34	266.71	407.69
Density (25°C; g/cm ³)	2.88	2.44	3.29	3.98
Critical temperature (°C)	—	354	499	682

^a Thermochemical data from J. Chao *et al.*, *JANAF Thermochemical Tables*, U.S. Department of Commerce, National Bureau of Standards (1965), 3rd Addendum (1968).

^b Boiling point of liquid.

^c To monomers AlF_3 .

^d To dimers Al_2X_6 .

TABLE 3

STRUCTURAL DATA FOR DIMERIC ALUMINUM, TRIHALIDES
 Al_2X_6

(Ref. 1)

Halide	MX bond lengths (Å)		XMX bond angles (°)	
	Bridging	Terminal	Bridging	Terminal
$Al_2Cl_6^*$	2.21	2.06	79	118
$Al_2Br_6^*$	2.33	2.21	87	115
$Al_2I_6^*$	2.58	2.53	102	112

* Interatomic distances, *Chemical Society Special Publication* 11 (1958) M25.

TABLE 4

ENTHALPIES OF FORMATION AND ESTIMATED BOND ENERGY TERMS $E(\text{Al-X})$ (kcal/mole) FOR THE Al-X BONDS OF SPECIES Al_2X_6^a

(Ref. 1)

	Cl	Br	I	H	Me
$-\Delta H_f^\circ (\text{Al}_2\text{X}_6)_{\text{est}}$	309	232	124		35
$E(\text{Al-X})_{\text{average}}$	69	60	46	41	36
$E(\text{Al-X})_{\text{terminal}}$	91	77	62	65	61

^a K. Wade, *J. Chem. Educ.* 49 (1972) 502.

TABLE 5

THERMOCHEMICAL DATA AND INTERATOMIC DISTANCES FOR GASEOUS MONOMERIC ALUMINUM TRIHALIDES AlX_3^a

(Ref. 1)

	AlF_3	AlCl_3	AlBr_3	AlI_3
$-\Delta G_f^\circ (25^\circ\text{C}; \text{kcal/mole})$	283	136	108	60
$-\Delta H_f^\circ (25^\circ\text{C}; \text{kcal/mole})$	287	140	101	49
$S^\circ (25^\circ\text{C}; \text{cal deg}^{-1} \text{mole}^{-1})$	66	75	85	87
$-\Delta H_{\text{reorg.}} (\text{kcal/mole})^b$	26	15	14	12
$\Delta H_{\text{reorg.}} (\text{kcal/mole})^b$	—	32	28	19
$E(\text{Al-X}) (\text{kcal/mole})^c$	—	102	86	68
$r(\text{Al-X}) (\text{\AA})$	1.63	2.14	2.27	2.44

^a J. Chao *et al.*, *JANAF Thermochemical Tables*, U.S. Department of Commerce, National Bureau of Standards (1965), 3rd Addendum (1968).^b Enthalpy change for the gas-phase process $\text{AlX}_3 \rightarrow \frac{1}{2}(\text{Al}_2\text{X}_6)$.^c Reorganization energy—energy required to deform the molecules from the planar to a pyramidal shape (XAlX angle 109°), as calculated by F. A. Cotton and J. R. Lato, *J. Chem. Phys.* 30 (1959) 993.^d Bond energy terms, from K. Wade, *J. Chem. Educ.* 49 (1972) 502.

TABLE 6

VIBRATIONAL SPECTROSCOPIC DATA FOR DIMERIC
ALUMINUM TRIHALIDES $Y_2AlX_2AlY_2$

(Ref. 1)

				Al_2F_6	Al_2Cl_6	Al_2Br_6	Al_2I_6
A_g	ν_1	Al-Y stretch	R	(939)	501	417	348
	ν_2	Al-X stretch	R	(602)	336	210	148
	ν_3	AlY ₂ scissoring	R		217	140	95
	ν_4	ring deformation	R		115	70	56
A_g	ν_5	AlY ₂ twist		(191)			
B_{1g}	ν_6	Al-X stretch	R	(874)	438	354	(301)
	ν_7	AlY ₂ wag	R	(326)	168	85	82
B_{1g}	ν_8	Al-Y stretch	IR	995s	625s	502s	415s
	ν_9	AlY ₂ rock	IR	340w	(194)		
	ν_{10}	ring puckering	IR			(18)	(13)
B_{2g}	ν_{11}	Al-Y stretch	R	(970)	608	485	405
	ν_{12}	AlY ₂ rock	R	(259)	(142)	114	63
B_{2g}	ν_{13}	Al-X stretch	IR	600w	420m	345m	291s
	ν_{14}	AlY ₂ wag	IR	(232)	(114)	90m	64vw
B_{2g}	ν_{15}	AlY ₂ twist	R	(336)	(163)	(103)	54
B_{2g}	ν_{16}	AlY stretch	IR	805m	484s	375s	320s
	ν_{17}	ring deformation	IR	575w	(375)	198s	140m
	ν_{18}	AlY ₂ scissoring	IR	300w	(175)	111mw	81w

Frequencies are in cm^{-1} . Vibrations are numbered according to the system of R. P. Bell and H. C. Longuet-Higgins, *Proc. Roy. Soc. (London)* A183 (1945) 357. R, Raman; IR, infrared; s, strong; m, medium; w, weak. Frequencies in parentheses are values calculated from normal coordinate analyses. For the gas-phase Raman spectra of Al_2X_6/AlX_3 mixtures (X = Cl, Br or I) see I.R. Beattie and J. R. Horder, *J. Chem. Soc. (A)* (1969) 2655.

* Data for Al_2F_6 assume D_{2h} symmetry and consist of estimated gas-phase frequencies based on frequencies observed for matrix-isolated species; A. Snelson, *J. Phys. Chem.* 71 (1967) 3202.

* Data relate to gaseous Al_2Cl_6 , from V. A. Maroni, D. M. Gruen, R. L. McBeth and E. J. Cairns, *Spectrochim. Acta*, 26A (1970) 418. See also T. Onishi and T. Shimanouchi, *Spectrochim. Acta*, 20 (1964) 325.

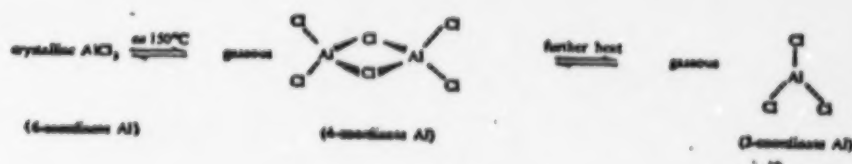
* For Al_2Br_6 and Al_2I_6 , infrared data relate to Nujol mulls, Raman data to solid samples, from I. R. Beattie, T. Gilson and G. A. Ozin, *J. Chem. Soc. (A)* (1968) 813.

b) Anhydrous Aluminum Fluoride, AlF_3

Aluminum fluoride is very inert. It does not react with cold water in which it is almost insoluble, or with boiling sulfuric acid. Water at $400^\circ C$ and fused KOH attack it only slowly. Aluminum fluoride reacts with sodium fluoride in the presence of a weak acid to give Na_3AlF_6 . Aluminum fluoride is soluble in hydrofluoric acid. AlF_3 has the giant network structure of ReO_3 .

c) Anhydrous Aluminum Chloride AlCl_3

Anhydrous aluminum chloride is very hygroscopic and fumes in moist air. In the solid, liquid and gaseous states below 327°C , aluminum chloride exists as the dimer, Al_2Cl_6 . Above 327°C , appreciable dissociation occurs with the trichloride to the monomer, AlCl_3 . Dissociation is essentially complete at 1100°C (2).



In inert solvents such as carbon disulfide, aluminum chloride also exists as the dimer. In solvents that form reactive complexes, it exists as the monomer in dilute solution.

Anhydrous aluminum chloride reacts vigorously with water to form hydrogen chloride and aluminum oxychloride, AlClO , and it fumes strongly in moist air owing to the formation of hydrochloric acid vapor. Slow, partial hydrolysis of anhydrous aluminum chloride gives aluminum oxychloride.

Aluminum chloride is soluble in hydrochloric acid and organic solvents including ethyl ether, trichloromethane, tetrachloromethane and absolute ethanol.

5.2.1.2 Hydrated Aluminum Salts

a) Aluminum Fluoride Hydrates $\text{AlF}_3 \cdot \text{XH}_2\text{O}$

There are three well defined stoichiometric hydrates $\text{AlF}_3 \cdot n\text{H}_2\text{O}$ ($n = 1, 3$ or 9). The nonahydrate $\text{AlF}_3 \cdot 9\text{H}_2\text{O}$ crystallizes from aqueous AlF_3 at low temperatures and is unstable above 8°C . The trihydrate $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ can exist in two forms: a highly soluble metastable α -form obtained by the action of aqueous HF on aluminum below 25° and a β -form (stable at 25°C) of lower solubility.

5. CHEMISTRY OF ALUMINUM COMPOUNDS FOR SPRAY PYROLYSIS

5.1 Introduction

The important parameters that affect the-deposition of a wear resistant coating using the spray pyrolysis technique will be investigated in this chapter.

The naturally occurring anhydrous oxide corundum, Al_2O_3 , is resistant to hydration and attack by acids. As one of the hardest substrates known (8.8 on Moh's scale), Carborundum is used as an abrasive powder, in abrasive papers, and in grinding wheels. Al_2O_3 has also been used as a wear resistant coating on tool bits.

Spray pyrolysis is a deposition process whereby a solution of compounds (usually salts) containing the cation(s) and anion(s) of interest is sprayed onto a hot substrate. The solution components react at the substrate surface to form a film or coating of the desired composition.

The substrate should be chemically and mechanically compatible with the Al_2O_3 coating. Because of the affinity of Al_2O_3 for oxides, it can be expected that glasses or ceramics will be the substrates of choice. For metallic substrates, an intermediate layer can be used to improve the adherence between the coating and the substrate. Coating adhesion can also be improved by various substrate surface treatments (see Chapter 3).

The temperature of the substrate for the deposition process is critical. If the temperature is too low, the sprayed droplets will splash on the substrate, vaporize, and leave a dry non-adhesive precipitate. If the temperature is too high, the compound will vaporize and decompose before it reaches the substrate. Again, the deposition will be non-adhesive. Ideally, the temperature of the substrate should be controlled such that the solvent vaporizes as the droplet approaches the substrate, then the solid melts and vaporizes (or sublimes) and the vapor diffuses to the substrate to undergo a heterogeneous reaction there.

The selected solvents used for spray pyrolysis should form a solution with the aluminum compounds. All the solute/solvent systems should be stable at room temperature. The chosen solvents in these solute/solvent systems should easily evaporate during the spraying process. The selected aluminum compounds (solutes) should have stable vapor phases and decomposition temperatures below the melting temperature of the substrates. Potential solute/solvent systems for the deposition of Al_2O_3 coating by spray pyrolysis will be evaluated in this chapter.

5.2 Aluminum Compounds

5.2.1 Inorganic Compounds

5.2.1.1 Anhydrous Aluminum Salts

a) Aluminum Halides

All halogens form binary trihalides with aluminum; aluminum chloride and fluoride are of more commercial importance than the bromide and iodide. Their physical properties and their thermodynamic data are listed in Tables 1 to 6.

TABLE 1
THE ALUMINUM HALIDES (Ref. 13)

	AlF_3	AlCl_3	AlBr_3	AlI_3
Appearance	Colourless, transparent triclinic crystals	Colourless hexagonal crystals. Very deliquescent	Colourless rhombic plates. Deliquescent	White crystals. Deliquescent
Lattice	ReO_3 structure	Slightly distorted CrCl_3 structure	Close-packed Br atoms with Al atoms in pairs of adjacent tetrahedral holes; hence a molecular lattice	
m.p. °C	1290	193	98	About 180
b.p. °C	Sublimes at 1290	Sublimes at 180	About 260	About 380
Structure of molecule in vapour		Dimeric; tetrahedral	Dimeric; tetrahedral	Dimeric; tetrahedral
Distance Al—X in ring		2.21	2.33	2.58
Distance Al—X in terminal positions		2.06	2.21	2.53
Solubility in water	0.56 gm in 100 gm at 25°	Soluble with violence	Soluble with violence	Soluble with decomposition
Hydrates (in terms of monomeric formulae)	0, 1, 3, 9	0, 6	0, 6, 15	0, 6
Specific conductivity $\times 10^4$ ohm ⁻¹ cm ⁻¹ of liquid at m.p.		0.45	0.09	1.2

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Aluminum alkoxides (eg. $\text{Al}(\text{C}_3\text{H}_7\text{O})_3$, $\text{Al}(\text{C}_2\text{H}_5\text{O})_3$) have been used to produce Al_2O_3 coatings by various methods including thermal decomposition, sol-gel and spray pyrolysis (Chapter 2.5)

Typical aluminum alkoxides include:

Aluminum isopropoxide $\text{Al}(\text{C}_3\text{H}_7\text{O})_3$ is a white solid with mp. at 128-133°C, b.p. at 125-130°C. It is easily soluble in aromatic and chlorinated hydrocarbons but sparingly soluble in alcohol.

Aluminum sec-butoxide $\text{Al}(\text{OC}_4\text{H}_9)_3$ is miscible with aromatic hydrocarbons (b.p. 180°C).

5.2.2.4 Other Organoaluminum Compounds (1)

Aluminum has an extensive organometallic chemistry. It can form metal derivatives $\text{R}_n\text{AlX}_{3-n}$ ($n = 1, 2, \text{ or } 3$) and anionic complexes M^+AlR_4^- with from one to four organic groups R sigma-bonded to the same metal atom. It can also apparently form weak π -complexes with certain olefins. Uniquely among the Group IV elements, it has a strong tendency to form electron-deficient alkyl or aryl bridges.

Aluminum acetyl acetonate is a volatile compound which melts at 192°C and boils at 315°C. Compounds of this type are nearly insoluble in water, easily soluble in alcohol, ether and benzene. They are monomeric in the vapor and in benzene solution.

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6. CHEMISTRY OF ZIRCONIUM COMPOUNDS FOR SPRAY PYROLYSIS6.1 Introduction

There are several complete compilations of the literature concerning zirconium up to about 1970⁽¹⁻⁶⁾. Several reviews of more limited scope have also been published, one on the structural aspects of zirconium chemistry⁽⁷⁾, on aqueous chemistry^(8,9) and ion-exchange properties of zirconium compounds⁽¹⁰⁾.

In Section 2.6 of this literature survey we discussed zirconia coatings, including preparatory routes, properties and applications. In this chapter we will deal with the chemistry of zirconium compounds in relation to the formation of these coatings. In particular preparatory routes that have been applied or could be potentially useful for spray pyrolysis will be singled out. The various coatings described, their preparatory routes, zirconia precursors, solvents when used and other reaction conditions are summarized in Table 6.1. It can be seen that relatively few "wet" methods have been employed. At first inspection the compounds of interest are a zirconium halide ($ZrCl_4$), a mixed halide alkoxide ($ZrCl_2(OC_2H_5)_2$), and an alkoxide (butylortho-zirconate). Thus, relatively few compounds have been utilized. In this survey of zirconium compounds for consideration in a spray pyrolysis set-up we will use the same criteria that were developed for precursors for alumina:

- (i) The ZrO_2 precursor should be soluble in a suitable solvent.
- (ii) The solute/solvent system should be stable at room temperature.
- (iii) The solvent should easily evaporate.
- (iv) The selected zirconia compounds should have stable vapor phases and decomposition temperatures below the melting temperatures of the substrate.

The pyrolysis reaction can be one of two general types:

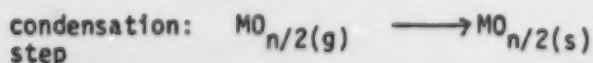
(a) Decomposition Reaction:

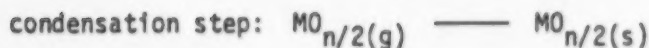
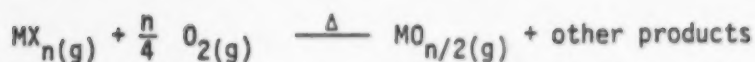
TABLE 6.1
Zirconium Compounds Used in Various
Methods for the Deposition of ZrO_2 Films

Technique	Coating Precursor	Solvent	Atmosphere/Temp	Substrate	Reference Ch. 2.6
Plasma Spray	ZrO_2 Powder	-		Ni-Ta	1
	Ni-Cr-Al-Y/ ZrO_2 - Y_2O_3 Powders	-		IN 625	2
Flame Spraying	ZrO_2 (CaO stab. powder) ZrO_2 rods + $AlPO_4$ binder	-		Ni-Mo-C alloy	3
				304 SS	4
Sputtering	ZrO_2 (12% Y_2O_3) powder	-			5
CVD	$ZrCl_4$ $Zr(tfacac)_4$	- -	CO_2+H_2 (800-1000°C) O_2 ($T > 400^\circ C$)	Si, SiO_2 Si	8 9
	$ZrCl_4 \cdot ZrCl_2(OC_2H_5)_2$ butyl ortho zirconate	C_2H_5OH butyl acetyl acetone	(120-800°C) Air	fused quartz Glass, SS	11 10
Reactive Evaporation	Zr	-	O_2 (10^{-4} Torr)	NaCl, mica	12
Doctor Blade Method	$ZrO_2(8\%Y_2O_3)$ powder	H_2O -5% methyl cellulose HNO_3	-	Zr rods, blocks and plates	14
Anodization			-	Zr foil	15, 16

(b) Combination Reaction:



or



6.2 Zirconium Compounds

Zirconium with titanium and hafnium occupy group IV B of the Periodic Table. The similarity between zirconium and hafnium is remarkable, the atomic radii are close (1.45 and 1.44 Å respectively). The differences with titanium are more pronounced, the most important one being that the lower oxidation states of Zr and Hf are relatively unimportant. The major oxidation state of Zr is +4. The chemistry of lower oxidation states is limited to non-aqueous chemistry of lower halides and some complexes thereof.

6.2.1 Inorganic Zirconium Compounds

6.2.1.1 Zirconium Tetrahalides

All four tetrahalides of zirconium are known. Equilibrium properties of the zirconium tetrahalides (and the similar hafnium tetrahalides) are reported in Tables 6.2 and 6.3.

Table 6.2

VAPOR PRESSURE RELATIONSHIPS FOR ZIRCONIUM AND
HAFNIUM TETRAHALIDES

Compound	$\log p = A - B/T$		Temperature (°K)	ΔH_v (kcal/mole)	Ref.
	A	B			
β -ZrF ₄	13.5571	12430	681-913	56.9 ± 0.2	(16)
α -ZrF ₄	12.150	10722	713-813	49.05	(207)
ZrCl ₄ (s)	11.766	5400	480-689	24.7 ± 0.3*	(415)
ZrCl ₄ (s)	11.83	5430	508-608	—	(196)
ZrCl ₄ (s)	11.4632	5191	<600	23.7 ± 1.0	(145)
ZrCl ₄ (l)	9.088	3427	710-741	—	(115)
ZrCl ₄ (l)	9.0421	3406	—	—	(66)
ZrCl ₄ (l)	9.4714	3730	711-773	—	(399)
HfCl ₄ (s)	11.712	5197	470-681	23.9 ± 0.3	(115)
HfCl ₄ (s)	11.64	5200	508-608	—	(196)
HfCl ₄ (s)	11.6726	5143	<600	23.5 ± 1	(145)
ZrBr ₄ (s)	12.402	5941	494-620	27.1 ± 2.2	(179)
HfI ₄ (s)	12.235	6214	530-674	28.37 ± 0.04	(538)
α -HfI ₄ (s)	19.46	10640	575-597	48.0 ± 1.3	(538)
β -HfI ₄ (s)	13.09	7370	598-645	33.7 ± 0.6	(538)
γ -HfI ₄ (s)	12.03	6125	646-678	28.2 ± 0.5	(538)
HfI ₄ (s)	9.0511	4261	548-605	26.0	(566)
HfI ₄ (s)	11.619	5814	605-668	—	(566)

* $\Delta H_v = 27.67 \pm$ kcal/mole as reported in JANAF Thermochemical Tables (Dow Chemical Company, Midland, Michigan) based on the data of Palko (415).

from Ref. 4

Table 6.3

PHYSICAL PROPERTIES OF ZIRCONIUM AND HAFNIUM TETRAHALIDES

Property	Ref.	ZrCl ₄	HfCl ₄	ZrBr ₄	HfBr ₄	ZrI ₄	HfI ₄
Melting point (°C)	(398)	435.5	433.2	450	424.5	500	449
	(415)	437	434	—	—	—	—
Critical temperature (°C)	(145)	503.5	482.5	532	473	666	643
	(391)	499	445	—	—	—	—
Triple point (°C)	(144)	437.3	432	—	—	—	—
	(399)	438.0	—	—	—	—	—
Critical density (gm/cm ³)	(398)	0.78	1.06	0.97	1.20	1.13	1.30
Vapor density (gm/cm ³)	(394, 567)	0.143	0.45	—	—	—	—
Liquid density (m.p.) (gm/cm ³)	(398, 145)	1.65	18.6	24.0	2.42	2.94	3.07
Critical pressure (atm)	(398)	57.4	54.0	42.9	40.5	40.7	39.0
ΔH_f° (kcal/mole)	(229)	-234.7	-236.7	—	—	—	—
	(199, 200)	-234.17 ± 0.29	-236.06 ± 0.29	—	—	—	—
ΔH_{vap} (kcal/mole)	(399)	17.1	—	—	—	—	—
	(415)	15.7 ± 0.9	—	—	—	—	—
ΔH_{fusion} (kcal/mole)	(415)	9.0 ± 0.9	—	—	—	—	—
	(145)	14 ± 3	18 ± 3	—	—	—	—

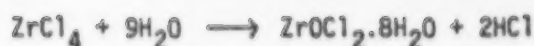
from Ref. 4

(a) ZrF_4 is a white crystalline solid which sublimates at 900°C .⁽¹¹⁾ Unlike the other halides ZrF_4 is insoluble in donor solvents. The compound is known to exist in three crystalline and one amorphous modification. Condensation of the tetrafluoride gas on a cool surface results in the formation of the α -form followed by the growth of crystals of the β -form. α - ZrF_4 may also be obtained by thermal decomposition of α - $\text{ZrF}_4 \cdot \text{NH}_4\text{F}$, and it may be stabilized by the addition of trivalent ions, such as Fe^{3+} or Ga^{3+} . Thermal decomposition of γ - $\text{ZrF}_4 \cdot \text{NH}_4\text{F}$ gives γ - ZrF_4 for $T \leq 400^\circ\text{C}$. The α , γ and amorphous forms transform irreversibly to the β -form at 400°C .

The vapor pressures above solid α - and β -zirconium tetrafluoride are described by the equations in Table 6.2 over the temperature ranges specified. The calculated heat of sublimation for the tetrafluoride of zirconium is some 20 kcal/mole greater than the heats of sublimation of the other tetrahalides of zirconium (Table 6.2), which is consistent with the greater complexity of the fluoride solid state compared to the probable structures of the other halides in the solid state. Zirconium tetrafluoride in the gaseous state is known to be monomeric by mass spectroscopy⁽¹²⁾. Fluorine bomb calorimetry has been used to determine the standard heats of formation of ZrF_4 : $-456.80 + 0.25 \text{ kcal}$ ⁽¹³⁾.

Zirconium tetrafluoride dissolves with difficulty in water. Dissolution in water at 100°C gives upon evaporation $\text{ZrF}_4 \cdot 3\text{H}_2\text{O}$ ⁽¹⁴⁾. The preparation of monohydrates was also attempted. Products of the composition $\text{ZrF}_4 \cdot n\text{H}_2\text{O}$ for which $n > 1$ were always produced, however. The trihydrate when heated in air to 80°C gave a product with $n = 1.14$. Vacuum at 80°C for 3 hours gave $\text{ZrF}_3.99 \cdot 0.59 \text{ H}_2\text{O}$. Simultaneous loss of HF and H_2O occurred by heating the 1.14 hydrate in vacuum till 200°C ⁽¹⁵⁾. Maricic et al. reported that dehydration of the 3-hydrate at 100°C gives the stoichiometric monohydrate⁽¹⁶⁾. Dehydration of the monohydrate in an atmosphere of HF at 400°C will yield βZrF_4 ⁽¹⁷⁾.

(b) ZrCl_4 is a white solid, subliming at 331°C and melting at 438°C under 25 atm. pressure. ZrCl_4 vapor is monomolecular but the liquid and solid state have complex monomolecular structures. Zirconium tetrachloride reacts violently and irreversibly with water, forming zirconyl chloride.



The product dissolves in liquid sulfur dioxide, molten stannous chloride, and molten alkali metal zirconates, from which it may be recovered by heating and volatilization (6)

Zirconium tetrachloride forms stable if readily hydrolyzable adducts with alcohols, amines, ammonia, esters, ethers, ketones, nitriles, nitrosyl chloride, phosphorus oxychloride, phosphorus pentachloride (but not phosphorus trichloride), and a large number of other Lewis bases. Some examples are $\text{ZrCl}_4 \cdot 9 (\text{CH}_3)_2\text{SO}$, $\text{ZrCl}_4 \cdot 2\text{HMPA}$ (hexamethylphosphoramide), $\text{ZrCl}_4 \cdot 2\text{CH}_3\text{CN}$, $\text{ZrCl}_4 \cdot 2\text{C}_2\text{H}_5\text{CN}$, $\text{ZrCl}_4 \cdot 2\text{C}_6\text{H}_5\text{SeO}$, $\text{ZrCl}_4 \cdot \text{COCl}_2$, $\text{ZrCl}_4 \cdot \text{SOCl}_2 \cdot \text{SOCl}_2$, and $\text{ZrCl}_4 \cdot 2 (\text{C}_4\text{H}_9)_3\text{PO}_4$. (6)

(c) ZrBr_4 is chemically very similar to the tetrachloride. ZrI_4 is similar in some respects, but is less stable and is oxidizable by dry air or oxygen at relatively low temperatures, about 200°C . The tetrabromide sublimes at 356°C , and has been melted under pressure at 449°C . When the tetraiodide is heated to about 1200°C , it breaks down to lower iodides and finally deposits zirconium metal (6).

6.2.1.2 Other Zirconium Halides and Derivatives

- (a) ZrF_3 can be prepared by the action on HF on ZrH_4 . It dissolves in organic acids and hot water without decomposition (25).
- (b) ZrF_2 has been prepared by the reduction of thin films of ZrF_4 with atomic hydrogen at about 350°C . It is a black solid which ignites in air to form ZrO_2 . At 800°C it disproportionates to zirconium metal and ZrF_4 (26).
- (c) ZrCl_2F_2 has been prepared by the reaction of $\text{ZrCl}_4 \cdot 2\text{PCl}_5$ with AsF_3 . This white crystalline substance hydrolyzes in water (27).
- (d) Fluorozirconic Acid Derivatives

It is convenient to regard zirconium tetrafluoride as analogous to an acid anhydride. The addition of hydrogen fluoride forms a complex acid:



and similarly the oxozirconium fluorides form oxofluorozirconic acids. Many such acids are known: H_2ZrF_6 ; $\text{H}_2\text{ZrF}_6 \cdot \text{H}_2\text{O}$; $\text{H}_2\text{ZrF}_6 \cdot 0.7\text{H}_2\text{O}$, $\text{HZrF}_5 \cdot 3\text{H}_2\text{O}$, $\text{HZrF}_5 \cdot 1.5\text{H}_2\text{O}$, H_2ZrOF_4 , $\text{H}_2\text{ZrO}_2\text{F}_2 \cdot \text{H}_2\text{O}$, HZr_2OF_7 from H_2ZrOF_4 heated above 345°C , and $\text{H}_2\text{Zr}_3\text{O}_4\text{F}_{10}$. Also the phases of composition $\text{ZrO}_{0.67}\text{F}_{2.67}$, $\text{ZrO}_{0.46}\text{F}_{3.08}$, $\text{ZrO}_{0.44}\text{F}_{3.12}$, and $\text{ZrO}_{0.25}\text{F}_{3.50}$, have been observed (6).

Fluorozirconates are most commonly prepared by heating zircon or zirconium dioxide with an alkali fluorosilicate:



or by evaporating solutions in which a fluoro-zirconic acid and an alkali fluoride have been dissolved.

- (e) K_2ZrF_6 is a colorless salt which melts at about 840°C . It dissolves in water to the extent of 1.22 g/100 g of water at 10°C , and 23.53 g/100 g at 100°C , giving a solution with a pH of about 4. The great variety of fluoro-zirconates that has been reported is indicated by Table 6.4.
- (f) $\text{KZrOF}_6 \cdot 2\text{H}_2\text{O}$ has been made by boiling aqueous potassium hexafluoro-zirconate with an appropriate addition of potassium hydroxide (28,29). Fluoro-zirconates are known to increase the durability of beryllium lead aluminum fluoride optical glass and to improve the corrosion resistance of metals (6).
- (g) ZrCl_3 : This compound dissolves in water with the formation of colored solutions. There is a rapid decoloration due to oxidation of Zr(III) to Zr(IV) by the water with the liberation of O_2 . ZrCl_3 forms adducts with monodentate and bidentate ligands, e.g. $\text{ZrCl}_3 \cdot 2$ pyridine and $2\text{ZrCl}_3 \cdot 5 \text{CH}_3\text{CN}$ (6).

Table 6.4

The Variety of Fluorozeonates

Anion	Cations forming salts with the anion (moles water per atom Zr)
ZrF_6^{4-}	Na, Na(H ₂ O), K, K(H ₂ O), Rb, Cs, Cs(H ₂ O), Tl, NH ₄ (H ₂ O), K + 0.5Ni(4H ₂ O), Mg(5H ₂ O), Zn, Mn(5H ₂ O), Ni(5H ₂ O), pyridinium, hydrazinium
ZrF_5^{3-}	Li, Li + Na, Na, K, K + Na, K + 0.5Cu(3H ₂ O), Cs, NH ₄ , Ba, Sn(II), Ni(12H ₂ O)
ZrF_4^{2-}	Li, Na, K, Rb, Cs, NH ₄ , Tl, Cu(8H ₂ O)
ZrF_3^{1-}	Li, Cu(12H ₂ O), Zn(12H ₂ O), Cd(7H ₂ O), Mn(6H ₂ O), Ni(12H ₂ O)
ZrF_2^{0-}	6 Li + Be
ZrF_2^{0-}	Li, Na, Rb
$Zr_2F_{11}^{3-}$	Na
$Zr_2F_{10}^{2-}$	Na, K
$Zr_2F_{10}^{2-}$	Cs(2H ₂ O), Cu(16H ₂ O)
$Zr_2F_{10}^{2-}$	Cs
$Zr_2F_{11}^{3-}$	Tl, Tl(H ₂ O)
$Zr_2F_{10}^{2-}$	Li
$Zr_2F_{11}^{3-}$	Na
$HOZrF_4^{3-}$	NH ₄ + H, K + H, Tl + H, Cs + H, 0.5Cd + H(2H ₂ O)
$ClZrF_4^{3-}$	Na, K
$OZrF_4^{3-}$	K, K(2H ₂ O)

from Ref. 6

- (h) $ZrBr_3$ and ZrI_3 are generally similar to the trichloride. The triiodide has been prepared by reducing zirconium tetraiodide with zirconium powder at 510°C, under pressure. It disproportionates at 360-390°C to zirconium diiodide and zirconium tetraiodide⁽⁶⁾.
- (i) $ZrCl_2$ is prepared by the disproportionation reaction of zirconium trichloride on heating to 650°C, or by reducing zirconium trichloride with sodium. It dissolves in molten aluminum trichloride, and it forms adducts with 2,2'-bipyridyl and 1,10-phenanthroline. Zirconium dibromide is generally similar to the dichloride.
- (j) $ZrCl$ is not a salt but a metallic phase containing one interstitial chlorine atom per zirconium atom. It is formed by electrolyzing a molten mixture of strontium and sodium chlorides in which zirconium tetrachloride is dissolved. X-ray diffraction study has shown it to consist of planes of zirconium atoms separated by the interstitial chlorine. The metallic properties of the zirconium are dominant. The composition does not dissolve in water, dilute hydrochloric acid, or common organic solvents. Bromine and iodine analogs are also known.

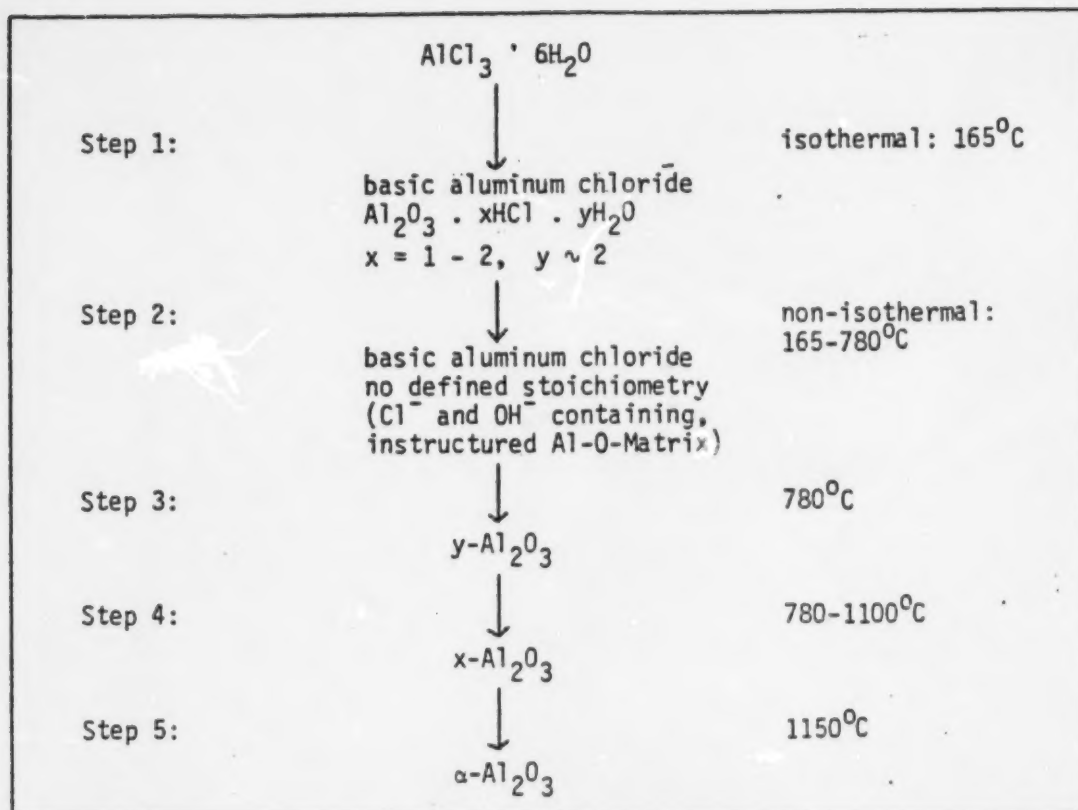


Figure 3: (Ref. 5)

c) Aluminum Nitrate $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$

Nonahydrate $\text{Al}(\text{NO}_3)_3$ is a white crystalline material, m.p. 73.5°C , soluble in cold water, alcohol and acetone. Decomposition to nitric acid and basic aluminum nitrates ($\text{Al}(\text{OH})_x(\text{NO}_3)_y$ ($x + y = 3$)) begins at 130°C and dissociation to aluminum oxide and oxides of nitrogen occurs above 500°C .

d) Aluminum Sulphate $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$

The solubility of aluminum sulphate is subject to considerable uncertainty because of the many poorly characterized hydrated salts that can be precipitated from aqueous solution. Solubility data for the $\text{Al}_2(\text{SO}_4)_3\text{-H}_2\text{O}$ system compiled by Seidel⁽⁶⁾ and by a commercial company⁽⁷⁾ are listed in Table 7.

The dehydration of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ has been shown to proceed in two distinct stages using DTA-TGA⁽⁸⁾. All but three molecules of water are lost between 40 and 250°C and the final three water molecules are lost between 250 and 450°C. $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$ is obtained by heating at 150°C; at 160°C the product is the hexahydrate $\text{Al}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$. Decomposition of the anhydrous salt to $\delta\text{-Al}_2\text{O}_3$ and SO_3 occurs between 580 and 900°C.

TABLE 7
ALUMINUM SULFATE IN AQUEOUS SOLUTION (Ref. 2)

Temperature, °C	Saturated solution, g $\text{Al}_2(\text{SO}_4)_3$ / 100 g H_2O , %*	
0	27.5	23.9
10	27.6	25.1
20		26.6
25	27.8	
30	28.0	28.8
35	28.4	
40	28.8	31.4
50	29.9	34.2
60	31.0	37.2
70	32.8	39.8
80		42.2
82	36.6	
90		44.7
95.1	41.9	
100		47.1
103.2	46.9	

* First column from Ref. 7; second column from Ref. 2.

5.2.1.3 Other Inorganic Aluminum Compounds⁽³⁾

The simple ion Al^{3+} will not be found in anhydrous salts or in binary compounds. Other aluminum salts include: aluminum hydroxide (a weak base), the aluminum salts of weak acids such as the carbonate, nitrite, cyanide, formate and acetate, either cannot be prepared, or are at once hydrolyzed in solution. The salts of strong acids such as the chlorate, perchlorate, nitrate, sulphate are stable. They are soluble in water and form hydrates with six or more molecules of water of crystallization. The compound most likely to contain the ion Al^{3+} would be anhydrous aluminum perchlorate. Aluminum perchlorate is very soluble in water and it crystallizes from the solution with 6, 8 and 15 H_2O molecules.

Other compounds are aluminum double salts and nitride, carbide, sulphide and phosphide salts. Al_4C_3 reacts with water or dilute acids to give methane and a little hydrogen. $\text{Al}_2(\text{C}_2)_3$ reacts with water to yield pure acetylene. AlN (stable up to 1800°C) is hydrolyzed by cold water to aluminum hydroxide and ammonia. It yields aluminum chloride and ammonia when heated in hydrogen chloride at 900°C and aluminum chloride and nitrogen when heated in chlorine at 300°C . AlP is readily hydrolyzed to give phosphine. It neither melts nor decomposes when heated to 2000°C .

5.2.2 Organic Compounds

5.2.2.1 Alkyl and Aryl Aluminum Compounds^(2, 3)

R_3Al compounds are colourless liquids or low melting solids easily oxidized and hydrolyzed when exposed to the atmosphere. The aluminum alkyls are alkyl-bridged dimers R_6Al_2 when R is ethyl, propyl, or n-butyl. The compounds are essentially monomeric when R is branched (e.g. isopropyl, isobutyl). Some of the alkyls and aryls of aluminum are listed in Table 8.

TABLE 8

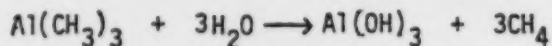
THE ALUMINUM ALKYLs, ARYLs, AND
THEIR DERIVATIVES

(Ref. 3)

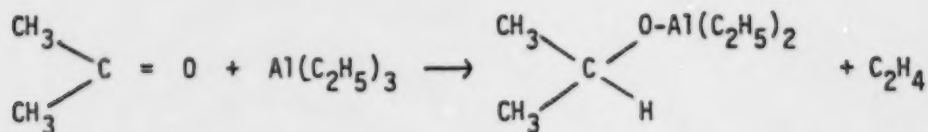
		m.p. °C	b.p. °C		
Dimeric	{	$\text{Al}(\text{CH}_3)_3$	+15	126.1	Dimeric at 70° 12% dimeric at 150°
		$\text{Al}(\text{C}_2\text{H}_5)_3$	-52.5	185.6	
		$\text{Al}(\text{i-C}_3\text{H}_7)_3$	-107	ca. 250	
		$\text{Al}(\text{C}_6\text{H}_5)_3$	230		
		$\text{Al}(\text{CH}_3)_2\text{N}(\text{CH}_3)_2$	154	228	Dimorphic
		$\text{Al}(\text{CH}_3)_2\text{SCH}_3$	103		
		$\text{Al}(\text{CH}_3)_2\text{Cl}$	{ -21 -45	119.4	
		$\text{Al}(\text{CH}_3)_2\text{Br}$	0	150	
		$\text{Al}(\text{CH}_3)_2\text{Br}_2$	79		
		$\text{Al}(\text{C}_6\text{H}_5)_2\text{Cl}_2$	94		
		$\text{Al}(\text{CH}_3)_2\text{Cl}_2$	73		
		$\text{Al}(\text{CH}_3)_2\text{I}_2$	70		
		$\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}_2$	32		
		$\text{Al}(\text{C}_2\text{H}_5)_2\text{I}_2$	39	158/4 mm	
Trimeric	{	$\text{Al}(\text{CH}_3)_2 \cdot \text{P}(\text{CH}_3)_2$	220	ca. 250	
		$\text{Al}(\text{CH}_3)_2 \cdot \text{OCH}_3$		ca. 140	
Tetrameric	{	$\text{Al}(\text{OCH}_3)_3$			
		$\text{Al}(\text{OC}_2\text{H}_5)_3$	139	320	
		$\text{Al}(\text{O iso-C}_3\text{H}_7)_3$	125	242/10 mm	
		$\text{Al}(\text{OC}_6\text{H}_5\text{CH}_2)_3$	81		

The dimeric and trimeric compounds in this list are reluctant to become monomeric; they are little dissociated at 150° and 30 mm.

Trimethyl aluminum slowly decomposes at 300°C, one of the products being methane. The lower alkyls are spontaneously inflammable in air, and they are violently attacked by water to give saturated hydrocarbons:



The aluminum alkyls react with ketones thus:



On hydrolysis, the product gives the secondary alcohol. At 110-115° trimethyl aluminum dissolves alkyls of the alkali metals to give conducting solutions, probably containing salts such as $\text{Na}\{\text{Al}(\text{C}_2\text{H}_5)_4\}$.

Triphenyl aluminum is easily soluble in benzene. It is oxidized by air in the solid state and in solution but less readily than the alkyl compounds.

5.2.2.2 Alkyl Aluminum Halides

$\text{R}_3\text{Al}_2\text{X}_3$ (X = Cl, Br, I; R = methyl, ethyl, propyl, i-butyl, etc.) are less easily oxidized and hydrolyzed than the trialkyls and triaryls. They are usually dimers with halogen bridges.

5.2.2.3 Aluminum Alkoxides

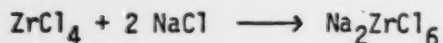
Aluminum alkoxides have the general formula $\text{Al}(\text{OR})_3$ when OR is an alkoxy group.

Aluminum alkoxides are easily soluble in hydrocarbons and chlorinated hydrocarbons, but sparingly soluble in alcohols. They are sensitive to moisture and dry storage is essential. They react with water to yield aluminum hydroxide and the alcohol.

- (k) M_2ZrCl_6 - Hexachlorozirconates are well known and have been widely studied. M^+ may be a univalent ion, including the tetraalkylammonium ion.

Cesium hexachlorozirconate has been crystallized from hydrochloric acid solutions and ammonium, potassium, and rubidium hexachlorozirconates from water solutions. The cesium and rubidium compounds are stable at 1000°C . The ammonium compound begins to decompose at about 450°C (6).

The hexachlorozirconates are most commonly prepared by heating zirconium tetrachloride with an alkali metal chloride under anhydrous conditions:



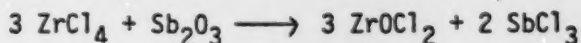
- (l) $ZrOCl_2$ is a colorless crystalline compound, usually forming tetragonal needles prepared by the hydrolysis of $ZrCl_4$.

Pure grades are prepared by recrystallizing from hydrochloric acid or methanol, or by preparation from pure intermediates. It is stable as the octahydrate at 20°C at 9.75-13.23 mm water vapor pressure. At other pressures, hydrates from about 4-9 moles of water per formula weight have been observed. The unit of structure in the crystalline octahydrate is a tetramer, to which four moles of water are bound at each zirconium atom, and to which an additional four moles of water and two moles of $H+Cl^-$ are held without covalent bonding to the core. The core zirconium atoms can be complexed by ligands other than water. Insoluble adducts have been precipitated from solution in formamide, dimethylformamide, acetamide, dimethylacetamide, acetanilide, benzylamide, methylacetamide, and acetone.

X-ray scattering by aqueous zirconyl chloride shows the persistence of the core structure of the crystal in the aqueous solution. Four chloride ions (and similarly bromide in zirconyl bromide solution) are not bound to the zirconium atoms, but are held in definite

positions along the sides of the square formed by the sets of four zirconium atoms. The behaviour of zirconium in aqueous zirconyl chloride solution is typical for a complex cation.

Anhydrous zirconyl chloride, ZrOCl_2 , cannot be prepared by dehydration of the hydrates. It has been prepared by the reaction of zirconium tetrachloride with antimony trioxide at 180-320°C (54.3):



and by the reaction of zirconium tetrachloride with chlorine monoxide in anhydrous carbon tetrachloride at -30°C. It is a white crystalline solid which decomposes at 250°C. It forms adducts with phosphorus oxychloride and with pyridine.

- (m) Basic Zirconyl Chlorides are compounds which contain less than two Cl atoms per Zr atom. The following examples have been reported⁽⁶⁾:

$\text{ZrO}_5\text{Cl}_4 \cdot 14\text{H}_2\text{O}$: very soluble in water

$\text{Zr}_2\text{O}_3\text{Cl}_2 \cdot \text{XH}_2\text{O}$: useful in precipitating dyes to form pigments

$\text{ZrOOHCl} \cdot \text{XH}_2\text{O}$: active principle in body deodorants

$\text{Zr}_2\text{O}_3\text{OHCl} \cdot \text{XH}_2\text{O}$

The latter three compounds are miscible with water in all proportions.

6.2.1.3 Zirconium Oxides

The main oxide formed by zirconium or hafnium is the dioxide MO_2 , whilst the unstable monoxide MO can be obtained in the gaseous state and lower oxides, e.g. Zr_3O and Zr_6O have been reported.

The phase diagram for the zirconium-oxygen system has been determined (30) and it was found that oxygen dissolved in the metal (α -form) forming solid solutions over the range $\text{Zr-ZrO}_{0.29}$. There was no evidence for the formation of ZrO as a separate phase. Recently it has been claimed (31) that Zr_6O and Zr_3O exist as ordered structures, both behaving as semiconductors.

ZrO -The monoxide has been detected spectroscopically in the sun and the stars and it appears to be the volatile oxide species obtained by heating either ZrO_2 or Zr/ZrO_2 mixtures. From mass spectra the heat of vaporization $\Delta H_v(\text{ZrO})_{2300^\circ} = 155 \text{ kcal}\cdot\text{mol}^{-1}$, the dissociation energy $D_{\text{Zr-O}} = 184 \text{ kcal}\cdot\text{mol}^{-1}$ (32).

ZrO_2 -The dioxide is naturally occurring as the mineral baddeleyite and is usually contaminated with some zircon, silica and oxides of iron aluminum and titanium. Methods of purifying ZrO_2 and also of obtaining it from zircon are well documented (1,3,6).

There are three well-established polymorphs - monoclinic, tetragonal and cubic, but the transition temperatures, which are sensitive to impurities, are not accurately known. For ZrO_2 : monoclinic $\leftrightarrow$ tetragonal $\sim 1100^\circ$, tetragonal $\leftrightarrow$ cubic $\sim 1900^\circ$. The monoclinic forms contain 7-coordinated metals (fig. 6.1) and in the tetragonal base-trigonal base polyhedron for ZrO_2 the Zr-O bond distances are: tetragonal base, 2.15-2.28 Å; trigonal base, 2.05-2.16 Å (33). The structural relationships between the zirconium dioxide polymorphs have been discussed (33). The cubic form of ZrO_2 may be obtained with a small particle size by thermolysis of zirconium tetraalkoxides (34).

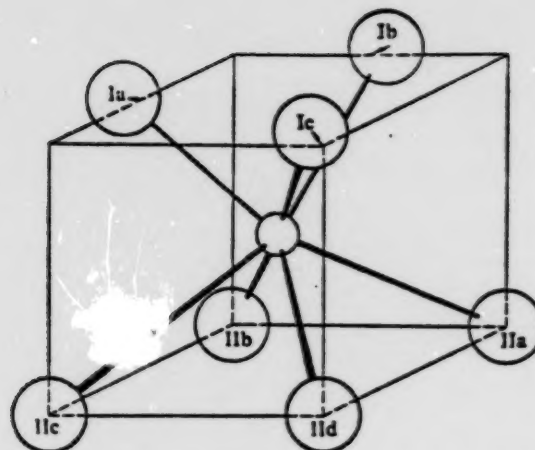


Fig. 6.1 Monoclinic ZrO_2 (baddeleyite). Small circle = zirconium atom; large circles = oxygen atoms.

From Ref. 5

A number of physical properties of ZrO_2 are presented in Table 6.5.

Table 6.5: Physical Properties of ZrO_2

	ZrO_2
Melting point ($^{\circ}\text{K}$)	2670
Boiling point ($^{\circ}\text{K}$)	4548
Density: Monoclinic	5.85
Tetragonal	6.16
Unit cell parameters ($\text{\AA}$): Monoclinic	$a=5.169$ $b=5.232$ $c=5.341$ $\beta=80^{\circ}45'$
Tetragonal	$a=5.085$ $c=5.166$
Cubic	$a=5.1$
Heat of formation (kcal mole^{-1})	-262.3
Heat capacity ($\text{cal deg}^{-1} \text{mole}^{-1}$)	$11.62 + 10.46 \times 10^{-5}T - 1.777 \times 10^{-8}T^2$
Refractive index: Monoclinic	2.15
Tetragonal	>2.15
Magnetic susceptibility (g^{-1})	-0.112×10^{-6}
Coefficient of thermal expansion (deg^{-1}):	
Monoclinic	$\sim 7 \times 10^{-6}$
Tetragonal	$\sim 12.8 \times 10^{-6}$
Transition temperature, Monoclinic-tetragonal ($^{\circ}\text{K}$)	1478
Heat of transition (kcal mole^{-1})	1.42

* JANAF Thermochemical Tables, Dow Chemical Company, Midland, Michigan (1967).

* P. Pascal, *Nouveau traité de chimie minérale*, Tome IX, Masson, Paris (1963).

* J. Lefèvre and R. Collongues, *Bull. Soc. Chim. France* (1961) 74.

* J. D. McCullough and K. N. Trueblood, *Acta Cryst.* 12 (1959) 507.

* E. J. Huber and C. E. Holley, *J. Chem. Eng. Data* 13 (1968) 252.

From Ref. 5

The ignited oxide is fairly unreactive. At high temperatures (800-1500°C) reaction with various metal oxides and salts takes place (3).

The high melting point, high refractive index, low coefficient of thermal expansion and high electrical resistivity have made ZrO_2 an important refractory material and of use as a ceramic opacifier and ceramic insulator. The phase change (monoclinic $\rightarrow$ tetragonal) at about 1100°C may be troublesome but the incorporation of a few per cent of calcium or yttrium oxides gives the cubic form and provides a "stabilized zirconia" which has useful refractory properties up to $> 2000^\circ$. The oxide also has catalytic properties either alone or as a promoter for hydrocarbon cracking and a variety of other organic reactions.

ZrO_2 is insoluble in HCl , HNO_3 and dilute H_2SO_4 but dissolves in hot concentrated H_2SO_4 and in HF (6). It reacts at moderately elevated temperatures with $(NH_4)_2SO_4$ to form water-soluble ammonium sulfatozirconate, with alkali fluorosilicates to form water-soluble ammonium sulfatozirconate, and with alkalies to form zirconates.

There are patents on wear-resistant products prepared by hydrogen reduction of ZrO_2 (18) and carbon reduction of ZrO_2 - TiO_2 mixtures (19). The use of ZrO_2 for a number of applications in the glass and ceramics industry is well known.

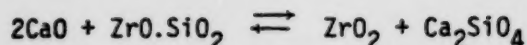
During the middle of the nineteenth century, zirconia found use as a glower in gas-light mantles; it was later replaced by thoria. Early in the present century, its usefulness as a ceramic opacifier was demonstrated, and other physical properties were exploited in abrasives, refractories, cements, and fillers. It improved heat resistance when dispersed in certain alloys. Latterly, uses have been developed as components of ceramic stains, components of ceramic elements used in fuel cells and other electrical systems, catalysts, starting material in making zirconium metal and alloys, and internal bonding agent dispersed in rubber and plastics. Zirconia fibers have been prepared, titanium dioxide pigment has been surfaced with zirconium dioxide to enhance its

stability in organic vehicles, and the resistance of glass to water, acids, and alkalies has been improved by the incorporation of zirconia. Stabilized zirconia, which contains calcium oxide, rare earth oxide, or occasionally certain other oxides in solid solution, has cubic crystalline symmetry, and is advantageously used in refractories. The crystalline inversion of the unstabilized oxide at about 1200°C leads to failures when ceramic objects are heated or cooled past this temperature (6).

Next to zircon (ZrSiO_4), zirconium dioxide commands the largest market of all zirconium compounds. A number of preparatory routes for zirconium dioxide are available.

- (i) Extraction from baddeleyite: This is the natural source of ZrO_2 . Separation from contaminants has not yielded a product of better quality than the recovery of this compound from zircon. The extraction of ZrO_2 from pure baddeleyite, a by-product of copper mining operations at Phalabova, South Africa has been an exception⁽⁶⁾.
- (ii) From zircon: Basically there are two major processes. Kinzie and co-workers boiled the silica out of zircon in an arc furnace⁽²⁰⁻²²⁾. Mixtures of zircon and carbon were heated in a furnace, silicon monoxide was evolved and pigs of zirconium carbide or cyanonitride were recovered. Subsequent combustion in air gave ZrO_2 . In an alternative process^(23,24) zircon is heated with alkali. The differences in solubility of SiO_2 and ZrO_2 from the reaction product in acid or alkali are then used to separate these components. Zirconia is usually prepared from the acidic solution by precipitating a pure basic sulfate, drying and firing it to volatilize water and sulfur trioxide to recover a residue of pure ZrO_2 .
- (iii) From ZrCl_4 : Combustion and steam hydrolysis of ZrCl_4 is known to give ZrO_2 .
- (iv) From zircon and calcium oxide - This process has proven particularly useful for the preparation of calcia-stabilized cubic zirconia. Zircon is heated with sufficient CaO (or other alkaline earth metal oxides) to 1250°C or higher. The calcium zirconylosilicate, CaZrSiO_5 formed

initially, breaks down to ZrO_2 , and Ca_2SiO_4 . The overall reaction can be written as:



Four per cent CaO or more is sufficient to produce calcia-stabilized cubic zirconia. The Ca_2SiO_4 can be separated by elutriation or sieving⁽⁶⁾.

- (v) High purity ZrO_2 - Extremely pure zirconia which is rather expensive has been prepared by a number of processes. Commonly it is prepared by the pyrolysis of zirconium compounds which are readily prepared in a very pure state, e.g. α -hydroxycarboxylates⁽³⁵⁾, recrystallized zirconyl chloride, and distilled zirconium alkoxides⁽³⁴⁾.

Higher Oxides - The reaction of ZrO_2 with carbon in vacuo gives ZrO and Zr_2O_3 , zirconium sesquioxide. The structure of Zr_2O_3 is face-centred cubic with $a = 4.62\text{\AA}$ ⁽³⁶⁾. Compounds of composition Zr_8O and Zr_6O are formed when oxygen dissolves in zirconium metal⁽³⁷⁾. A phase of composition Zr_5O_{24} has also been detected by X-ray diffraction⁽³⁸⁾.

Hydrous ZrO_2 - Addition of hydroxide to zirconium (IV) solutions causes the precipitation of white gelatinous $\text{ZrO}_2 \cdot n\text{H}_2\text{O}$, where the water content is variable; no true hydroxide exists. Hydrous zirconia is useful as an anion-exchange substrate in acidic environments and as a cation-exchange substrate in alkaline environments. Hydrous zirconia precipitates as particles with diameters of the order of 25 microns. Modifications, designated α , β and γ are distinguished by decreased chemical activity in the stated order⁽³⁹⁾. When a slurry of hydrous zirconia is boiled for a long period, the initial amorphous structure changes to that of monoclinic zirconium dioxide in an acidic environment and to that of cubic zirconium dioxide in an alkaline environment. The process is more rapid when carried out in an autoclave⁽⁴⁰⁾.

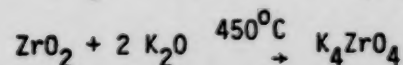
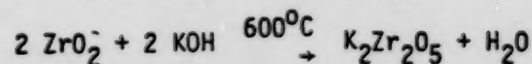
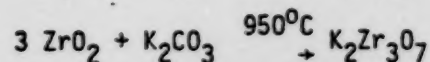
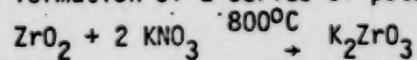
If the precipitated amorphous hydrous zirconia is filtered, washed, dried, and heated slowly, it inverts to tetragonal zirconium dioxide at about 400°C. It still retains about one per cent of water, by weight. On further heating, it inverts to monoclinic zirconium dioxide, at 600-800°C. With this inversion, all identity as hydrous zirconia has disappeared, but traces of water persist to about 1000°C.

Hydrous zirconia is insoluble in water, but soluble in strong mineral acids and insoluble in low concentrations of strong alkalines. It is insoluble in weak acids and weak alkalines. At high concentrations of strong alkaline hydrozirconate ions, Zr(OH)_5^- and Zr(OH)_6^{2-} are formed (41).

Hydrated peroxides are precipitated if H_2O_2 is present in alkaline solutions of zirconium compounds. An example is $\text{ZrO}_3 \cdot 2\text{H}_2\text{O}$ (1). Water soluble peroxozirconates form, such as $\text{Na}_4\text{Zr}_2\text{O}_{11} \cdot 9\text{H}_2\text{O}$, $\text{K}_4\text{Zr}_2\text{O}_{11} \cdot 9\text{H}_2\text{O}$ and Na_2ZrO_6 with the addition of excess strong alkalies.

6.2.1.4 Zirconates

A group of compounds named zirconates may be formed by combining oxides, hydroxides, nitrates, etc., of other metals with similar zirconium compounds and firing the mixtures at 1000-2500°C. The zirconates are mixed metal oxides, like their titanium analogues. No discrete zirconate ions are known. An example is the formation of a series of potassium zirconates (6).



Zirconates that have been reported in the literature are listed in Table 6.6.

Table 6.6
Zirconates Reported in the Literature (Ref. 6)

BaZrO ₃	La ₂ Zr ₂ O ₇	Rb ₂ Zr ₂ O ₇
CaZrO ₃	Li ₂ ZrO ₃	Rb ₂ Zr ₂ O ₇
CeZr ₂ O ₇	Li ₂ Zr ₂ O ₇	Sm ₂ Zr ₂ O ₇
Cs ₂ Zr ₂ O ₇	Li ₄ ZrO ₄	SrZrO ₃
Fe ₂ ZrO ₄	Na ₂ ZrO ₃	Sr ₂ Zr ₂ O ₁₀
K ₂ ZrO ₃	Nd ₂ Zr ₂ O ₇	Sr ₂ Zr ₂ O ₇
K ₂ Zr ₂ O ₄	PbZrO ₃	Sr ₂ ZrO ₄
K ₂ Zr ₂ O ₇	Pr ₂ Zr ₂ O ₇	Y ₂ Zr ₂ O ₇
K ₂ Zr ₂ O ₁₇		Yb ₂ Zr ₂ O ₇
K ₄ ZrO ₄		

Zirconates of bivalent metals usually have perovskite structures but compounds of the type $M^{II}ZrO_4$ having the spinel structure are also known.

6.2.1.5 Inorganic Zirconium Salts

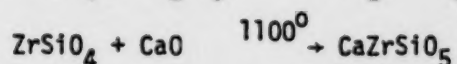
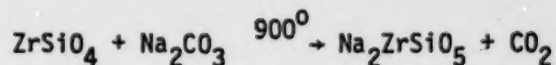
As many inorganic metals, the possibilities for salt formation with zirconium as the cation are numerous. The subject has been reviewed elsewhere (1,3,5,6). Only those classes of inorganic salts that are potentially useful for spray pyrolysis will be reviewed here. An exception is zircon, $ZrSiO_4$ which by itself may be a useful candidate material for an abrasion resistant coating.

Zircon, $ZrSiO_4$

The best known zirconium silicate is zircon, $ZrSiO_4$, which is very hard, highly refractive, birefringent and refractory (1,3).

It has a macromolecular structure containing 8-coordinated zirconium (dodecahedral; $Zr-O = 2.15, 2.29 \text{ \AA}$) and is stable to about 1540° when it dissociates to $ZrO_2 + SiO_2$ which will recombine if allowed to cool slowly. Rapid quenching produces a mixture of monoclinic zirconium dioxide and vitreous silica.

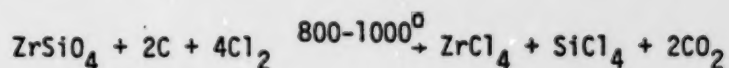
Zircon reacts with alkalis and alkaline earths at high temperatures forming metal zirconium silicates.



The mineral is generally unreactive to acids but is attacked by concentrated sulphuric acid at high temperature and pressure.

It is attacked by fluorides such as hydrogen fluoride, potassium bifluoride, potassium hexafluorosilicate, etc., being converted to the complex zirconium fluoride and silica.

Chlorination in the presence of carbon at high temperature gives the tetrachloride.



The physical properties of zirconium silicates are collected in Table 7.7.

Table 7.7

Physical Properties of Zirconium Silicates (from Ref. 5)

Property	ZrSiO ₄	Complex silicate
Melting point (°C)		Na ₂ ZrSi ₂ O ₇ , 1470° Rb ₂ ZrSi ₂ O ₇ > 1350°
Transition temperature (°C)		NaHZrSiO ₅ , 300° Na ₂ ZrSi ₂ O ₇ , 1120° Na ₂ Zr ₂ Si ₂ O ₉ , 850°
Heat capacity (cal deg ⁻¹ mole ⁻¹)	31.48 + (3.92 × 10 ⁻³)T (-8.08 × 10 ⁵)T ⁻² (25-1500°) ^a	
Density	4.7 (α) ² 3.9-4.0 (γ) ²	Rb ₂ ZrSi ₂ O ₇ , 3.84°
Resistivity (ohm cm)	9.9 × 10 ¹³ (200°) ^a 2.2 × 10 ¹⁰ (450°) ^a	
Dielectric constant	12 (17-22°) ¹ 8.51 (450°) ^a	
Zr-O bond length (Å)	2.15, 2.29°	

^a V. M. Polezhaev, V. M. Ust'yantsev and V. G. Chukhlantsev, *Russ. J. Inorg. Chem.* 11 (1966) 567.

^b V. G. Chukhlantsev and K. V. Alyamovskaya, *Izv. Akad. Nauk SSSR, Neorgan. Materialy* 1 (1965) 1994; *CA* 64 (1966) 7651e.

^c Y. M. Polezhaev and V. G. Chukhlantsev, *Russ. J. Inorg. Chem.* 9 (1964) 615.

^d J. P. Coughlin and E. G. King, *J. Am. Chem. Soc.* 72 (1950) 2262.

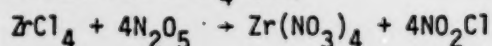
^e J. E. Comeforo and R. A. Hatch, *J. Am. Ceram. Soc.* 37 (1954) 317.

^f *Handbook of Chemistry and Physics*, 50th edn., Chemical Rubber Co., Cleveland, Ohio (1969-70).

^g I. R. Krstanovic, *Acta Cryst.* 11 (1958) 896.

Nitrates

Two nitrates have been known for many years. The hydrated tetranitrate $\text{Zr}(\text{NO}_3)_4(\text{H}_2\text{O})_5$ is obtained from strong nitric acid below 15° but zirconium oxynitrate $\text{ZrO}(\text{NO}_3)_2(\text{H}_2\text{O})_2$ is more readily obtained. Other hydrates of these two nitrates have also been reported and hafnium forms analogous compounds (1,3). Recently, the anhydrous tetranitrate $\text{Zr}(\text{NO}_3)_4$ was obtained from the reaction of dinitrogen pentoxide with ZrCl_4 (42)



Zirconium tetranitrate decomposed at 140° , but like the anhydrous hafnium tetranitrate which was isolated as the complex $\text{Hf}(\text{NO}_3)_4(\text{N}_2\text{O}_5)$ it could be sublimed at 100° in vacuo (43). Although solution studies indicated the possible existence of anionic species $\text{M}(\text{NO}_3)_5^-$ and $\text{M}(\text{NO}_3)_6^{2-}$ no double nitrates have yet been reported.

Related compounds that have been prepared are:

- (i) basic nitrates, e.g. $\text{Zr}(\text{OH})_2(\text{NO}_3)_2(\text{H}_2\text{O})_4$
- (ii) bis-chelated metal dinitrates, e.g. $\text{Zr}(\text{diket})_2(\text{NO}_3)_2$
- (iii) alkoxy mono-chelated metal dinitrates, e.g. $\text{Zr}(\text{OR})(\text{diket})(\text{NO}_3)_2$ and related compounds.
- (iv) cyclopentadienyl metal nitrates, e.g. $(\text{C}_6\text{H}_5)_2\text{Zr}(\text{NO}_3)_2$

Carbonates

The only compound of importance in this class is $(\text{NH}_4)_3\text{ZrOH}(\text{CO}_3)_3 \cdot 2\text{H}_2\text{O}$, ammonium tricarbonatozirconate or ammonium zirconyl carbonate. The commercial product is usually sold as an aqueous solution assaying about 10% ZrO_2 . It has been used as a component of water-repellent treatments for textiles, in floor polishes and in improving the water-resistance of the adhesive of paper coatings. It has been shown effective in improving the weather and abrasion resistance of acrylic latex paints and alginate films, and the adhesion of lithographic films to metal plates. Also, its use as an agent for deposition of zirconia films by the techniques of solution ceramics has been described (48).

Other Inorganic Salts

$\text{ZrP}_2\text{O}_7 \cdot (\text{H}_2\text{O})_5$, zirconium phosphate, is an insoluble solid which is prepared by adding a solution of zirconium oxychloride to a solution of phosphoric acid and drying the precipitate at 110°C (1,3). Ignition of zirconium phosphate ($1000\text{--}1400^\circ\text{C}$) produces the cubic ZrP_2O_7 (44). Further heating above 1550°C causes dissociation of phosphoric oxide leaving a residue of $\text{Zr}_2\text{P}_2\text{O}_9$ (1).

The sulphate ion has a strong affinity for zirconium as shown by the crystallization of the normal salt $\text{Zr}(\text{SO}_4)_2 \cdot (\text{H}_2\text{O})_4$ from aqueous sulphuric acid solutions and by the formation of a large number of anionic sulphato-complexes and basic sulphates. The tetrahydrate is converted to the monohydrate $\text{Zr}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ at 100°C which becomes anhydrous $\text{Zr}(\text{SO}_4)_2$ at 380°C (5).

Zirconyl perchlorate, $\text{ZrO}(\text{ClO}_4)_2 \cdot 8\text{H}_2\text{O}$ is a well-known compound, similar in chemistry to zirconyl chloride. Unlike zirconyl chloride, the perchlorate can be dehydrated completely without decomposition in vacuo over phosphorous pentoxide at 200°C (49). Other ligands can take the place of water.

6.2.2 Organic Zirconium Compounds

6.2.2.1 Carboxylates

Carboxylato compounds of the type $\text{Zr}(\text{O}_2\text{CR})_4$, $\text{ZrO}(\text{O}_2\text{CR})_2(\text{H}_2\text{O})_x$ and $\text{ZrO}(\text{OH})(\text{O}_2\text{CR})(\text{H}_2\text{O})_x$ have been known for many years (1). The solubility in water decreases and the solubility in alcohol increases with increasing alkyl chain length. The thermal stability of the tetracarboxylates is not very great and breakdown to oxycompounds readily occurs (50).

$\text{Zr}(\text{CH}_3\text{CO}_2)_4$ has been prepared by boiling a mixture of zirconium tetrachloride or zirconium tetraethoxide and glacial acetic acid (51-53). The compound is soluble in benzene and decomposes in water with the formation of soluble products. $\text{H}_2\text{ZrO}_2 \cdot (\text{CH}_3\text{CO}_2)_2$, zirconyl acetate, is prepared by dissolving carbonated hydrous zirconia in its equivalence of acetic acid. It is miscible with water in all proportions. The product of commerce usually is an aqueous solution assaying 22% ZrO_2 . When the solution is dried, an amorphous residue is formed. This and other properties indicate the molecule to be a high polymer.

The chief uses of zirconyl acetate have been in rendering textiles water-repellent by aqueous or organic solvent applications, bonding protective compounds to textiles, catalyzing the cure of silicone resins applied to textiles, leather, and other materials, hardening gelatin used as a vehicle for photosensitive substances, and preparing extrudable dopes from which zirconia fibers can be manufactured (6).

$\text{Zr}_2\text{O}(\text{OH})(\text{CH}_3\text{CO}_2)_5 \cdot 2\text{H}_2\text{O}$ is formed when zirconyl chloride is boiled with an excess of nearly 100% acetic acid, followed by evaporation of the solution. It forms an anisotropic solid, $d_{25} = 1.963$, which is unstable in air. It has been observed to begin to decompose at 50°C , first losing one mole of acetic acid with the formation of crystalline $\text{Zr}_2\text{O}_2(\text{CH}_3\text{COO})_4 \cdot 2\text{H}_2\text{O}$. At 200°C , one mole of water and one-half mole of $(\text{CH}_3\text{CO})_2\text{O}$ per mole of zirconium are lost, leaving a product of composition $\text{Zr}_4\text{O}_5(\text{CH}_3\text{COO})_6 \cdot 2\text{H}_2\text{O}$. The loss of another mole of $(\text{CH}_3\text{CO})_2\text{O}$ above 275°C leads to $\text{Zr}_2\text{O}_3(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$. The final breakdown product, ZrO_2 is formed at $430\text{--}450^\circ\text{C}$ (4,54).

$\text{HZrOOH}(\text{HCO}_2)_2$, diformatozirconic acid, is prepared with difficulty from carbonated hydrous zirconia by dissolving it with formic acid. It is unstable, and has found no use. Evaporation of a solution of zirconyl chloride to which a large excess of formic acid has been added yields crystals of composition $\text{Zr}_2\text{OOH}(\text{HCO}_2)_5 \cdot 2\text{H}_2\text{O}$. They dissolve in water in all proportions, and are slightly soluble in alcohol, benzene, and chloroform, but insoluble in ether. The compound is stable in air at room temperature (55). Infrared studies indicate the formate ligand to be bidentate (56).

$\text{Zr}_2\text{O}(\text{OH}) \cdot (\text{HCOO})_5 \cdot 2\text{H}_2\text{O}$ is formed by adding zirconium oxychloride to a boiling solution of 85% formic acid. The compound is very soluble in water, and sparingly soluble in ethanol, benzene and chloroform. The compound loses 0.5 mole of water in the range $70 - 110^\circ\text{C}$, a mole of formic acid between $110 - 220^\circ\text{C}$ to give $\text{Zr}_2\text{O}_2(\text{HCOO})_4 \cdot 1.5\text{H}_2\text{O}$, and loses additional formic acid and water between $220 - 350^\circ\text{C}$ to yield $\text{M}_2\text{O}_3(\text{HCOO})_2$ (4).

Fatty Acid Derivatives

There have been many previous studies on zirconium compounds of the so-called "fatty acids", which upon analysis are usually found to be oxy species. For example, the reaction of excess steric or palmitic acids with the isopropyl alcohol solvate of tetraisopropoxide zirconium (57,58) in benzene at reflux temperatures gives final products which are consistent with the composition $[(RCOO)_3Zr]_2O$. Actually this reaction can be carried out so as to isolate the mono- and disubstituted alkoxides, $Zr(RCOO)(OPr^i)_3$ and $Zr(RCOO)_2(OPr^i)_2$.

Treatment of the disubstituted product with additional fatty acid in benzene gives products for which there is some evidence of decomposition, although one additional isopropoxide group can be replaced. Tetrasubstituted products were obtained when a suspension of zirconium tetrachloride in benzene was reacted with fatty acids at reflux temperatures. A slow evolution of hydrogen chloride was observed over a period of 14 hours, followed by the deposition of colorless crystals of the tetrasubstituted product.

6.2.2.2 Alkoxides

Much work has been carried out over the past 30 years on metal tetraalkoxides, $M(OR)_4$, and metal alkoxy compounds $MX_n(OR)_{4-n}$ and recent reviews are available (59, 60). The tetraalkoxides are co-ordination polymers $[M(OR)_4]_n$ ($n < 3.5$ for lower aliphatic R groups) due to bridging by alkoxide groups (see Table 6.8).

Accurate vapour pressures are known for the monomeric tert-butoxides and tert-amyl oxides and in principle zirconium and hafnium could be separated by fractional distillation or gas-liquid chromatography (Tables 6.9 and 6.10). Thermal stabilities are in the order $Zr(OMe)_4 \sim Zr(OEt)_4 \gg Zr(OPr^i)_4 \gg Zr(Obu^i)_4$, and high purity ZrO_2 of small particle size can be made by thermolysis (34,61). The alkoxides are readily hydrolysed and react with hydroxylic compounds, acids, β -diketones, etc.

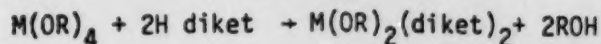
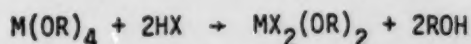


Table 6.8
Physical Properties of Quadrivalent Metal Alkoxides
(From Refs. 5, 59)

Compound	Degree of polymerization ^a	Volatility (°C/mmHg)	ΔH_{vap} (kcal mole ⁻¹)
Ti(OCH ₃) ₄	4.0 ^a	170 ^a /0.1	—
Ti(OC ₂ H ₅) ₄	4.0 ^a	138.3/5.0	21.6
Ti{OCH(CH ₃) ₂ } ₄	1.0 ^a	91.3/5.0	14.7
Ti{OC(CH ₃) ₃ } ₄	1.0	93.8/5.0	14.5
Ti{OSi(CH ₃) ₃ } ₄	1.21	111/10.0 ^a	13.7
Zr(OCH ₃) ₄	—	280/0.1 ^f	—
Zr(OC ₂ H ₅) ₄	3.6	234.8/5.0	30.2
Zr{OCH(CH ₃) ₂ } ₄	3.57	203.8/5.0	31.5
Zr{OC(CH ₃) ₃ } ₄	1.0	89.1/5.0	15.2
Zr{OSi(CH ₃) ₃ } ₄	2.05	135/0.1 ^a	—
Hf(OCH ₃) ₄	—	—	—
Hf(OC ₂ H ₅) ₄	—	~190/0.1	—
Hf{OCH(CH ₃) ₂ } ₄	3.33 ^a	170/0.35	—
Hf{OC(CH ₃) ₃ } ₄	1.0	90/6.5	—
Hf{OSi(CH ₃) ₃ } ₄	—	—	—

^a Tetrameric in the crystalline state (D. A. Wright and D. A. Williams, *Acta Cryst.* B24 (1968) 1107).

^b Tetrameric in the crystalline state (J. A. Ibers, *Nature* 197 (1963) 686); but trimeric in solution (D. C. Bradley and C. E. Holloway, *Inorg. Chem.* 3 (1964) 1163, contains other references).

^c n.m.r. spectra show polymerization at low temperatures (ref. 175).

^d Number average degree of polymerization in boiling benzene (ref. 171) unless otherwise specified.

^e Cryoscopic results in benzene (ref. 177).

^f D. C. Bradley and M. M. Faktor, *Nature* 184 (1959) 55.

^g D. C. Bradley and I. M. Thomas, *J. Chem. Soc.* (1959) 3404; also I. M. Thomas (Ph.D. thesis, London, 1959).

^h From refs. 174 and 175.

ⁱ From refs. quoted in (177); τ value (TMS = 10.000) of α -protons.

^j Chemical shift varies with temperature and concentration, see ref. (177).

^k τ value for the β -protons.

^l τ -value for β -protons for the freshly distilled compound (see ref. 177).

^m Si-O frequency not C-O.

Table 6.9 VAPOUR PRESSURES AND HEATS OF VAPORIZATION OF TITANIUM, ZIRCONIUM AND HAFNIUM TETRA-TERTIARY BUTOXIDES^a

Compound	Temp. (°K)	300	320	340	360	380	400
Ti(OCMe ₃) ₄	<i>P</i> (mmHg)	0.049	0.25	1.00	3.26	9.04	21.41
	ΔH_v (kcal mole ⁻¹)	15.8	15.2	14.7	14.1	13.5	13.0
Zr(OCMe ₃) ₄	<i>P</i> (mmHg)	0.066	0.34	1.35	4.42	12.30	29.77
	ΔH_v (kcal mole ⁻¹)	15.9	15.3	14.8	14.2	13.7	13.1
Hf(OCMe ₃) ₄	<i>P</i> (mmHg)	0.069	0.36	1.48	4.80	13.05	30.49
	ΔH_v (kcal mole ⁻¹)	16.3	15.5	14.7	13.9	13.2	12.4

^a Data from D. C. Bradley and J. D. Swanwick, *J. Chem. Soc.* (1958) 3207; (1959) 748.

Table 6.10 VAPOUR PRESSURES AND HEATS OF VAPORIZATION OF TITANIUM, ZIRCONIUM AND HAFNIUM TETRA-TERTIARY AMYLOXIDES *

Compound	Temp. (*K)	350	370	390	410	430	450
Ti(OCMe ₂ Et) ₄	P (mmHg)	0.117	0.44	1.41	3.89	9.55	21.14
	ΔH _v (kcal mole ⁻¹)	17.3	16.8	16.4	15.9	15.5	15.0
Zr(OCMe ₂ Et) ₄	P (mmHg)	0.126	0.52	1.77	4.98	12.13	26.01
	ΔH _v (kcal mole ⁻¹)	18.7	17.8	16.9	16.0	15.1	14.2
Hf(OCMe ₂ Et) ₄	P (mmHg)	0.134	0.55	1.84	5.24	12.98	28.53
	ΔH _v (kcal mole ⁻¹)	18.5	17.7	17.0	16.2	15.5	14.7

* Data from D. C. Bradley and J. D. Swanwick, *J. Chem. Soc.* (1958) 3207; (1959) 748.

The mechanism for the decomposition of zirconium tetratertiary butoxide to ZrO₂ powders, proposed by Mazdiyasi et al (61), is schematically represented in Fig.6.2.

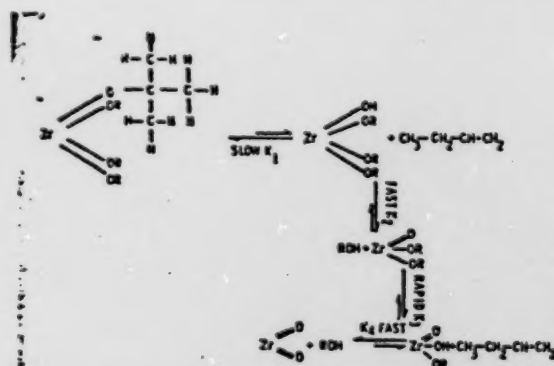
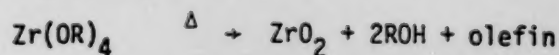


Fig. 6.2 Reaction mechanism of an alkoxide to oxide.

From Ref. 61

The products of the reaction are olefin, alcohol, and oxide. The rate of the equation is dependent on the concentration of the starting material. The rate equation as a function of concentration is:



$$V = kK_1[\text{Zr(OR)}_4]$$

Where V is rate of reaction, k is a proportionality constant, and K is the specific rate constant for the rate-controlling reaction step. Thermogravimetric analysis of zirconium isopropoxide indicates that this is a two-step decomposition in which the bound isopropyl is removed between 100° and 125°C and decomposition of the oxide is completed between 250° and 300°C . A TGA curve determined on a Stanton thermobalance in nitrogen atmosphere is shown in Fig.6.3. The compound decomposes slowly in a stream of dry nitrogen even at room temperature. The same compound in a sealed ampul decomposes slowly when exposed to light. The butoxides are slightly more stable (if they are in a solvent media such as benzene or tertiary butyl acetate) for a longer period of time, but decomposition still occurs fairly rapidly.

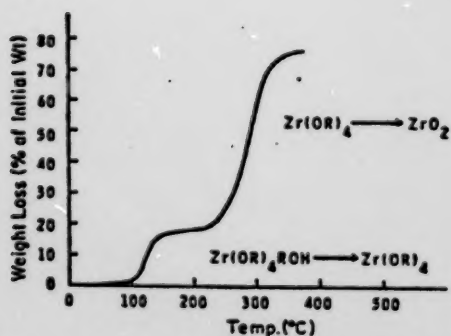


Fig. 6.3 Decomposition of zirconium alkoxides in N_2 atmosphere.

From Ref. 61

X-ray analysis of the zirconia powders suggested that cubic zirconia was present. The powders remained cubic during heat treatment up to 300°C . The transformation to the monoclinic phase started beyond this point and was virtually complete at 400°C . These X-ray results were confirmed by DTA (Figure 6.3, 6.4). Four successive runs are shown.

The runs show in general an endothermic peak at 1170°C upon heating and a corresponding large exothermic peak at 770°C upon cooling. It was postulated that the initial transformation must be from the fine particle cubic to tetragonal (1170°C) with enough crystallites remaining to induce the nucleation of the cubic phase on cooling. On prolonged heating (run 4) grain growth occurs which favors the tetragonal to monoclinic transformation (950-1100°C).

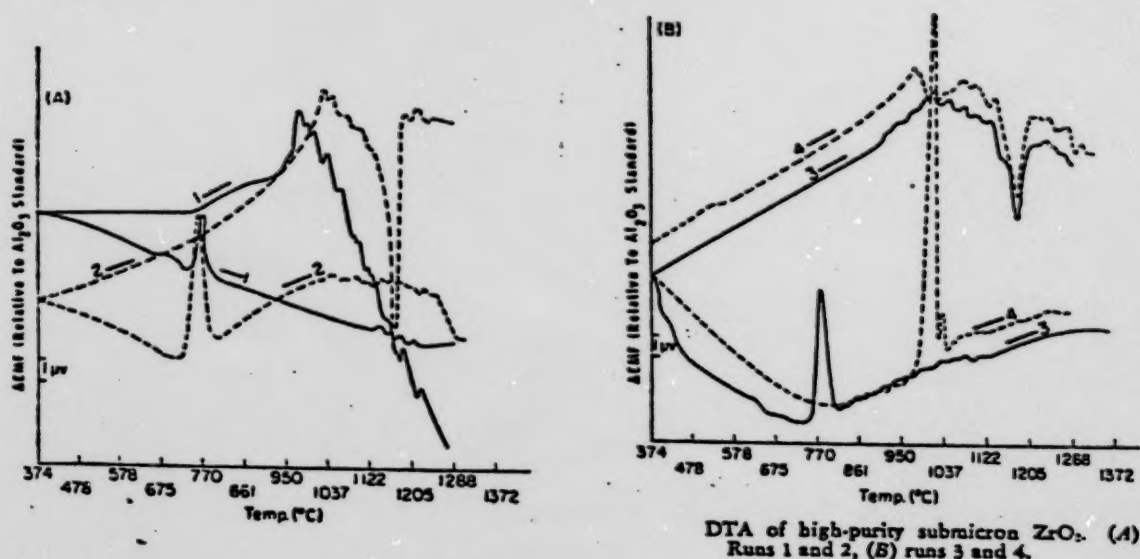


Fig. 6.4

6.2.2.3 Ethers, Ketones, Organic Oxides and Amides

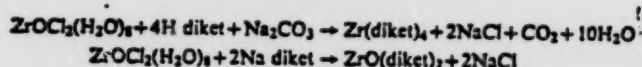
Ethers are poor bases for the metal tetrahalides. The $\text{ZrCl}_4 \cdot 2\text{E} + 2\text{O}$ adduct is known to decompose at 95°C (62). The adduct with acetone has the molecular formula $\text{ZrCl}_4 \cdot 2(\text{CH}_3)_2\text{O}$ (62) although it has also been reported (63) that at -5°C in carbon tetrachloride the 1:1 adduct is obtained. The room temperature reaction yields hydrogen chloride and $\text{Cl}_3\text{ZrCH}_2\text{COCH}_3$. With methylisopropyl ketone the product is $\text{Cl}_3\text{ZrCH}_2\text{COC}_3\text{H}_7$.

Dioxane forms a 1:1 adduct with ZrCl_4 (64). Certain cyclic ketones dissolved in acetyl chloride with ZrCl_4 gave a precipitate of 2:1 ketone: ZrCl_4 . The adducts have the following melting points: anthrone, m.p. $> 325^\circ\text{C}$; 10-nitro-anthrone, m.p. 251°C ; 10-benzalanthrone, m.p. 266°C ; benzanthrone, m.p. $> 300^\circ\text{C}$ (65).

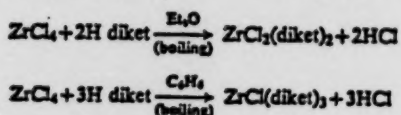
Ethers and sulfones do not react with ZrF_4 at $50\text{--}160^\circ\text{C}$, but 2:1 adducts of DMSO, N, N'-tetramethyl urea and DMF were formed upon refluxing a slurry of ZrF_4 in excess base (66). The DMF complex has a melting point of $206\text{--}208^\circ\text{C}$ (67).

6.2.2.4 Diketonates

Zirconium derivatives of the enolates of β -diketones of the general types $\text{ZrO}(\text{diket})_2$, $\text{Zr}(\text{diket})_4$, $\text{ZrX}(\text{diket})_3$, $\text{ZrX}_2(\text{diket})_2$, $[\text{Zr}(\text{diket})_3]\text{FeCl}_4$, $[\text{Zr}(\text{diket})_3]\text{AuCl}_4$ and $[\text{Zr}(\text{diket})_3]_2\text{P}(\text{Cl})_6$ (diket - enolate of 1,3-diketone; X = halide) have long been known (1,3,68). The zirconium oxy bis-diketonate and the tetrakis-diketonate can be prepared from aqueous solution:



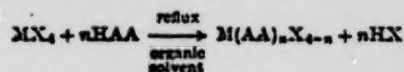
The other compounds are prepared by reactions in non-aqueous solvents:



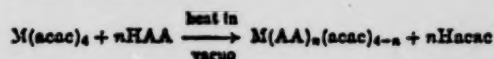
Five commonly used preparatory methods are listed in Table 6.11

Table 6.11 Common Preparatory Routes for the Synthesis of Metal Diketonate

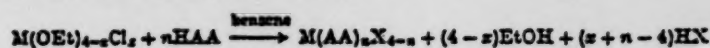
1. Metal tetrahalide and diketone



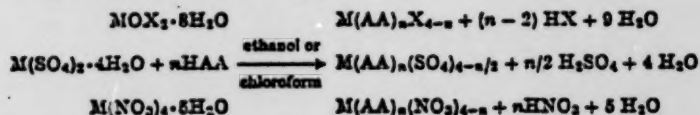
2. Metal chelate and diketone



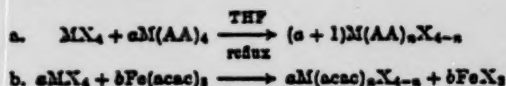
3. Metal alkoxide and diketone



4. Hydrated salt and diketone



5. Metal tetrahalide and chelate



from Ref. 4

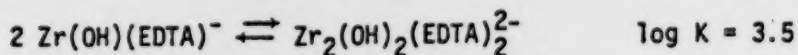
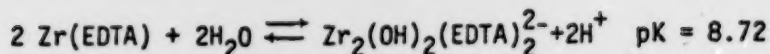
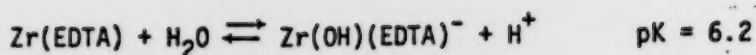
Diketonates of zirconium and the preparatory method are listed in Table 6.12

Table 6.12

from Ref. 4

TETRAKIS(DIKONATO)METALLATES $[M(AA)_4]$

Metal	Diketone anion	Melting point (°C)	Method of preparation ^a	Ref.
Zr	1,1,1-Trifluoro-2,4-pentanedionato	130-131	1 (CCl ₄)	(375)
	1,1,1,5,5,5-Hexafluoro-2,4-pentanedionato	39-42	1 (CCl ₄)	(102)
		152-154	1 (CCl ₄)	(374)
	2,2,6,6-Tetramethyl-3,5-heptanedionato	—	—	(160a, 511)
	1,3-Diphenyl-1,3-propanedionato	238-239	2, 3	(80, 594)
	1-p-Biphenyl-1,3-butanedionato	275-277	2	(594)
	1,3-Bis(p-biphenyl)-1,3-propanedionato	302-303	1	(594)
	1-Phenyl-3-p-biphenyl-1,3-propanedionato	254-255	3	(594)
	1,3-Bis(1-naphthyl)-1,3-propanedionato	278-277	3, 4	(594)
	1,3-Bis(2-naphthyl)-1,3-propanedionato	278-279	3	(594)
	1,2,3-Triphenyl-1,3-propanedionato	210-220	1	(594)
	3-Butyl-2,4-pentanedionato	131.5-133 (dec.)	2	(80)
	Tropolone	300 (subl.)	1	(379)
	Tropolone	300 (subl.)	1	(379)
Hf	1,3-Diphenyl-1,3-propanedionato	238-239	2	(594)
	1,1,1-Trifluoro-2,4-pentanedionato	130-131	1 (CCl ₄)	(375)
	1,1,1,5,5,5-Hexafluoro-2,4-pentanedionato	47.5-49.5	1 (CCl ₄)	(102)
	1-Phenyl-1,3-butanedionato	205.5-207.5	2	(86) -



The data suggests that the EDTA complex does not dissociate easily in aqueous solution.

6.2.2.7 Organometallic Compounds

A substantial amount of work has been carried out in the area of zirconium-carbon bonded compounds. The types of compounds can be grouped as follows:

- (i) alkyls and aryls
- (ii) allyls
- (iii) π -cyclopentadienyls and arenes
- (iv) carbonyls, nitrosyls and cyanides

Alkyl zirconium compounds are highly unstable. Tetramethylzirconium was prepared by the reaction of stoichiometric amounts of methyl-lithium and zirconium tetrachloride in an ether-toluene solvent mixture at -45°C (82). The red liquid product recovered at -30°C decomposes at -15°C with the evolution of methane and the formation of a black color. The substitution of methyl groups by cyclopentadienyl groups improves the stability, $(\pi\text{-C}_6\text{H}_5)_2\text{ZrCl}(\text{CH}_3)$ decomposes at $191\text{--}193^\circ\text{C}$ (83).

The reaction of pentafluorophenyllithium and $(\pi\text{-Cp})_2\text{ZrCl}_2$ in diethyl ether gives $(\text{-C}_6\text{F}_5)\text{Zr}(\pi\text{-C}_6\text{H}_5)_2$ (84). The reported melting point (257°C) does not agree with the 219°C (dec.) reported by Chaudari and Stone (85). The product reacts strongly with moisture to form ultimately $(\pi\text{-C}_6\text{H}_5)_2\text{Zr(OH)}_2$. The compounds tend to explode near or above their melting points.

Although bis-cyclopentadienyl zirconium dichloride was isolated in 1953, the tetrakis-cyclopentadienyl $\text{Zr}(\text{C}_5\text{H}_5)_4$ and bis-cyclopentadienyl $\text{Zr}(\text{C}_5\text{H}_5)_2$ were obtained only recently. The $\text{M}(\text{C}_5\text{H}_5)_4$ compounds are made from MCl_4 or $(\text{C}_5\text{H}_5)_2\text{MCl}_2$ and NaC_5H_5 . Spectroscopic data showed that all hydrogens are equivalent but structures have not been determined. These compounds react with protic reagents HL to give $(\text{C}_5\text{H}_5)_2\text{ML}_2$ and $(\text{C}_5\text{H}_5)\text{ML}_3$ derivatives (86-88).

The bis-cyclopentadienyl $\text{Zr}(\text{C}_5\text{H}_5)_2$ is a purple-black, pyrophoric, diamagnetic solid (sublimes $300^\circ/10^{-3}\text{mm}$) obtained from the reaction of $(\text{C}_5\text{H}_5)_2\text{ZrCl}_2$ with sodium and naphthalene in THF under helium (89).

Tetracyclopentadienyl zirconium is stable in air up to 75°C and in an inert atmosphere up to 400°C . It hydrolyzes to zirconium oxide in water and it gives $\text{Zr}(\text{OE}^+)_4$ with ethanol.

The cyclopentadienyl derivations of zirconium exchange easily with organic and inorganic ligands. For example, starting with ZrCp_4 , three of the four cyclopentadienyl groups may be substituted by chelating ligands. For a review of the exchange reaction see E.M. Larsen (4).

Substituted zirconium (and hafnium) diketonates are listed in Table 6.13

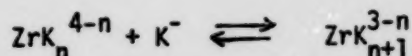
Table 6.13

from Ref. 4

SUBSTITUTED BIS AND TRIS CHELATES $[M(AA)_2X_2, M(AA)_3X]$

Metal	Diketone anion	X	Melting point (°C)	Method of preparation ^a	Ref.
$M(AA)_2X_2$					
Zr	2,4-Pentanedionato	Cl	180.5-182	1(Et ₂ O)	(174)
		Cl	236	1(Et ₂ O)	(131)
		Cl	68-78	5a	(194)
		Br	185-186.5	1(Et ₂ O)	(174)
Hf	2,4-Pentanedionato	Cl	186-188	1(Et ₂ O)	(174)
		Br	190-192	1(Et ₂ O)	(174)
		NO ₃	148-148.5	4	(86)
		Cl	271-273	5a	(80)
Zr	1,3-Diphenyl-1,3-propanedionato	Cl	231-234	5a	(194)
		NO ₃	254-256	4	(594)
		Zr(SO ₄) ₂	>350	4	(594)
		NO ₃	237-238	4	(86)
Hf	1,3-Diphenyl-1,3-propanedionato	NO ₃	132.5-134 (dec.)	5a	(80)
Zr	3-Butyl-2,4-pentanedionato	Cl	189.5-190	4	(86)
Hf	1-Methyl-3-phenyl-1,3-propanedionato	NO ₃			
$M(AA)_3X$					
Zr	2,4-Pentanedionato	Cl	134	1(benzene)	(131, 443)
		Cl	134-136	5b	(131)
		Cl	159.5-161	1(benzene)	(174)
		Cl	156-158	1(THF)	(80)
		Cl	143-148	1(CHCl ₃)	(148)
		Br	162.5-164	1(CCl ₄)	(174)
		I	178-183 (dec.)	5(THF)	(174)
		I	171-172	1(isopropylether)	(174)
		Cl	154-156	1(benzene) 5a, 5b	(131)
		Cl	159.5-161	1(benzene)	(174)
Hf	2,4-Pentanedionato	Br	161.5-163.5	1(benzene)	(174)
		NO ₃	157-157.5	1(benzene)	(86)
Zr	1-Phenyl-1,3-butanedionato	Cl	122-124	1(benzene)	(131)
Hf	1-Phenyl-1,3-butanedionato	Cl	125-128	1(benzene)	(174)
Zr	1,3-Diphenyl-1,3-propanedionato	Cl	262	3, 4	(594)
		Cl	256-258	1(benzene)	(131)
		Br	280	1(benzene)	(594)
		I	233	1(EtOH or CHCl ₃)	(594)
		NO ₃	237	1(benzene or EtOH)	(594)
		FeCl ₄	170	(CHCl ₃)	(131)
		AuCl ₄	—	(CHCl ₃)	(131)
		Cl	258-268	1(benzene)	(131)
Hf	1,3-Diphenyl-1,3-propanedionato	Cl	259	4	(594)
		Cl	261-262	5a	(86)
		Cl	255 (dec.)	1,3(benzene)	(594)
Zr	1-p-Biphenyl-1,3-butanedionato	Cl			

Peshkova et al (69 - 74) have calculated stability constants for the equilibria



for the β -diketones and related compounds. Successive formation constants of β -diketone chelates are given in Table 6.14. Conditions are: $T = 25^\circ\text{C}$, $\mu = 1.0$, metal ion concentrations from 10^{-6} - 10^{-7} mol. L^{-1} and $\text{pH} = 0-2$

Table 6.14

from Ref. 4

SUCCESSIVE FORMATION CONSTANTS OF β -DIKETONE CHELATES

	Ligand	$\log k_1$	$\log k_2$	$\log k_3$	$\log k_4$	Ref.
Zr	Bzac	12.71	11.86	11.34	11.08	(429)
	Acac	8.38	7.58	7.26	6.80	(328)
	Sta	11.35	10.17	10.05	9.25	(362)
	Na	12.11	11.82	11.09	10.37	(428)
	Tta	10.93	10.81	10.38	10.30	(363)
Hf	Bzac	11.68	11.29	10.28	10.78	(424)
	Acac	7.40	7.28	6.74	6.68	(425)
	Sta	10.46	10.28	9.48	9.48	(426)
	Na	11.61	11.07	10.96	10.57	(423)
	Tta	10.80	10.64	10.06	10.02	(426)
	Dbzin	12.42	11.63	11.37	10.97	(424)

The $k_1 - k_4$ values show that the formation of the highest complex is favourable under the conditions of the experiments.

$\text{Zr}(\text{C}_5\text{H}_7\text{O}_2)_4$, zirconium tetraacetylacetonate has a melting point of $194 - 195^\circ\text{C}$. It is prepared by the reaction of zirconylchloride with acetylacetone in aqueous solution. The compound is sparingly soluble in water, cyclohexane, and pinene; moderately soluble in acetone, 1-butanol, chlorobenzene, dimethylformamide, dioxane, nitrobenzene, and ethyl acetate, and highly soluble in benzene.

$\text{Zr}(\text{tfacac})_4$ and $\text{Zr}(\text{hfacac})_4$, where tfacac is trifluoroacetylacetonate and hfacac is hexafluoroacetylacetonate. These compounds are prepared by the reaction of ZrCl_4 and the appropriate ligand (75). The preparation involves adding 5.6 g of 5,2,6 - 6 - tetramethylhepta - 3,5 - dione slowly to a slurry of 1.1 g ZrCl_4 in 50 ml CCl_4 . These species have been used for the preparation of ZrO_2 films by CVD. The films could be obtained at temperatures as low as $450 - 550^\circ\text{C}$.

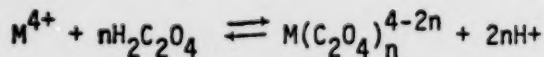
6.2.2.5 Dicarboxylates

Zirconium compounds of dibasic acids (especially oxalic) have long been known (1,3), e.g. $\text{Zr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_x$, $\text{ZrO}(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_x$, $\text{Zr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{C}_2\text{O}_4)(\text{H}_2\text{O})_8$, $\text{K}_4[\text{Zr}(\text{C}_2\text{O}_4)_4](\text{H}_2\text{O})_5$ and $(\text{NH}_4)_4[\text{Zr}(\text{C}_2\text{O}_4)_4](\text{H}_2\text{O})_6$. The oxy-derivatives ZrOL and K_2ZrOL_2 (L = malonate, malate, succinate, adipate, phthalate) have also been prepared.

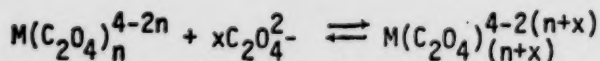
Basic oxalates, e.g. $\text{Zr}_{10}\text{O}_{11}(\text{OH})_{10}(\text{C}_2\text{O}_4)_4(\text{H}_2\text{O})_{53}$ and mixed oxalate complexes, such as $\text{K}_4\text{Zr}_2(\text{C}_2\text{O}_4)_5(\text{SO}_4)(\text{H}_2\text{O})_{10}$ have been prepared (5).

The zirconium (IV) oxalate ion system is the most thoroughly studied of the group.

The equilibrium constants for the formation of the species described in the equation



were obtained at 2 and 4 M hydrogen ion and metal ion concentrations of 5×10^{-6} M or less (76). At an ionic strength of 2.0, the equilibrium constants were, for zirconium $K_1 = 2.96 \pm 0.3 \times 10^5$ and $K_2 = 4.8 \pm 1.6 \times 10^9$. Successive equilibrium constants, defined by the net equation,



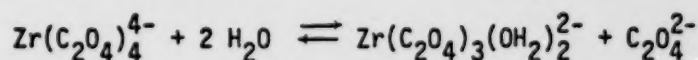
at pH 1.82, metal ion concentration of 4.8×10^{-5} M, and an ionic strength of 0.04 (20°C) were determined to be $K_1 = 1.35 \times 10^{11}$, $K_2 = 1.5 \times 10^9$, $K_3 = 4.53 \times 10^6$, and $K_4 = 1.07 \times 10^6$. The maximum number of oxalates bound to the zirconium was only four. These values were obtained from data on the mobility of zirconium ions in perchloric acid and sodium perchlorate solutions as a function of the oxalate: zirconium ratio (77).

The normal neutral oxalate $\text{Zr}(\text{C}_2\text{O}_4)_2$ has been prepared (78) by adding stoichiometric quantities of oxalic acid to a solution of zirconium tetrachloride in absolute methanol. Only oxy species were obtained from aqueous solution.

A variety of methods have been used to prepare soluble tetraoxalato salts. A suitable synthesis for potassium tetraoxalato-zirconate (hafnate)⁽⁷⁹⁾ free of hydroxy species is one in which a zirconium (hafnium) oxychloride solution is added to a buffered solution containing a stoichiometric amount of potassium oxalate and half the amount of oxalic acid. The potassium tetraoxalatometallate pentahydrate is then precipitated upon slow addition of ethanol.

The tetraoxalato species of zirconium and hafnium when dissolved in water produce an instantaneous increase in the hydrogen ion concentration and a corresponding quantity of a hydroxylated metallate species. In addition to hydrolysis, an aquation reaction is also likely.

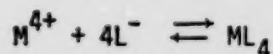
A tentative value for the equilibrium constant for the reaction



was found to be about 10^{-4} (78).

6.2.2.6 Aminopolycarboxylic Acids

EDTA: Intorre and Martell⁽⁸⁰⁾ report the presence of a 1:1 Zr^{4+} : EDTA complex in solution ($[\text{Zr}^{4+}] = 2.5 \times 10^{-3} \text{ mol.L}^{-1}$). The same authors⁽⁸¹⁾ determined the formation constant for the equilibrium



to be $\log K = 29.0 \pm 0.05$.

The authors studied the hydrolysis and polymerization of the EDTA complex at metal ion concentrations of $(5 \text{ to } 40) \times 10^{-4} \text{ M}$. They arrived at the following equilibrium constants:

6.3 SUMMARY

The chemistry of zirconium is quite extensive and numerous compounds and routes are available. Using the following criteria a number of zirconium compounds and classes of compounds have been shortlisted for use as zirconia film precursors using the spray pyrolysis technique.

- a. Chemical stability: the compounds and their solutions must be sufficiently stable to prevent decomposition to polymerized species before the substrate surface is reached.
- b. Solubility: a suitable solvent or solvents must be available to dissolve the zirconia precursor. Reaction between solute and solvent should be of a limited nature. Coordination complexes are allowed, but extensive polymerization should be avoided.
- c. The species should be present in the gasphase, preferably as a single molecular species, prior to reaching the substrate surface.
- d. It should be commercially available or easily prepared.

Table 6.15 lists the compounds that are potentially useful ZrO_2 precursors. Broadly speaking these compounds are the halides, the carboxylates, the alkoxides, the diketonates and the aminocarboxylic acid derivatives.

Table 6.15 Zirconium Compounds for Use in Spray Pyrolysis

Compound or Class of Compounds	References
	Chapter 6
ZrCl_4	6
ZrBr_4	6
ZrI_4	6
$(\text{NH}_4)_2\text{Zr OH}(\text{CO}_3)_3 \cdot 2\text{H}_2\text{O}$	48
$\text{Zr}(\text{CH}_3\text{CO}_2)_4$ and derivatives	4,6,50,54
$\text{Zr}(\text{OR})_4$	5,34,59,61
$\text{Zr}(\text{acac})_4$	6
$\text{Zr}(\text{tfacac})_4$	75
$\text{Zr}(\text{hfacac})_4$	75
$\text{Zr}(\text{EDTA})$	80,81

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APPENDIX B - SPRAY PYROLYSIS OF TIN OXIDE AT ORF**B1 History**

The Department of Metals, Glass and Ceramics has successfully completed two major projects on the spray pyrolysis of tin oxide coatings. Both projects were performed in conjunction with Day Specialties Company Ltd., Midland, Ontario. These projects involved the coating of glass and enamelled steel substrates by spray pyrolysis with a thin semiconducting tin oxide layer for the purpose of providing surface electrical conductivity and infrared reflectivity while remaining visibly transparent.

The first of the two successive projects progressed through several steps in the development process. These were:

- (a) Laboratory preliminary trials using hand spraying and minimal apparatus at ORF
- (b) Laboratory pilot trials using a specially constructed furnace and spray system. This apparatus was a combined manual and semi-automatic system.
- (c) Plant pilot trials were performed in an apparatus designed at ORF and constructed by the company. This system was significantly larger than the laboratory system and was almost fully automatic. Sufficient flexibility was built into the system to allow for the incorporation of process improvements. Laboratory pilot data supplemented the plant pilot system, especially in troubleshooting solution composition problems.
- (d) Full scale production facilities were designed and constructed by the company based on the experience gained in the pilot trial operations.

At ORF, the laboratory pilot facility was utilized for troubleshooting and new product development. At the end of these projects ORF decided to construct a fully instrumented spray pyrolysis facility in order to investigate a variety of chemical systems in addition to tin oxide. Experience gained in the previous laboratory trials allowed the identification and selection of critical control parameters as well as the critical process variables which had to be measured in order to correlate coating quality with the process conditions.

A specially designed and instrumented system was constructed. Instrumentation problems were accentuated by the fact that the spray pyrolysis step is typically in the range of 0.5 to 3 seconds. The special facilities are described in the next section.

B2 Spray Pyrolysis Apparatus at ORF

The spray pyrolysis system constructed by ORF consists of a furnace/spray booth assembly and an instrumentation and control system.

The furnace/spray booth system consists of a 1 cubic foot furnace with pneumatically operated lids and sample holder with a primary fume shroud contained in a negative pressure chamber. A schematic drawing of the furnace assembly is presented as Figure B-1. The spray system attached to the furnace assembly allows the control of atomization gas pressure, solution feed pressure, atomization air on/off time and solution on/off time. A pneumatic control schematic is presented as Figure B-2.

All timing and on/off control is performed by a dedicated microcomputer system. In addition to control timing functions, the microcomputer system acquires data during the spray process and stores it in mass storage (floppy disks) for post run analysis. Substrate temperature/time profiles were found to be critical in previous development work with tin oxide coatings. The substrate temperature can be measured using either a surface thermocouple or a non-contacting infrared pyrometer. System control functions are performed by TTL compatible solid state relays activating solenoid type pneumatic valves. The gas currently being used is air, however, other gases can be easily incorporated. A block diagram of the instrumentation and control system is presented as Figure B-3.

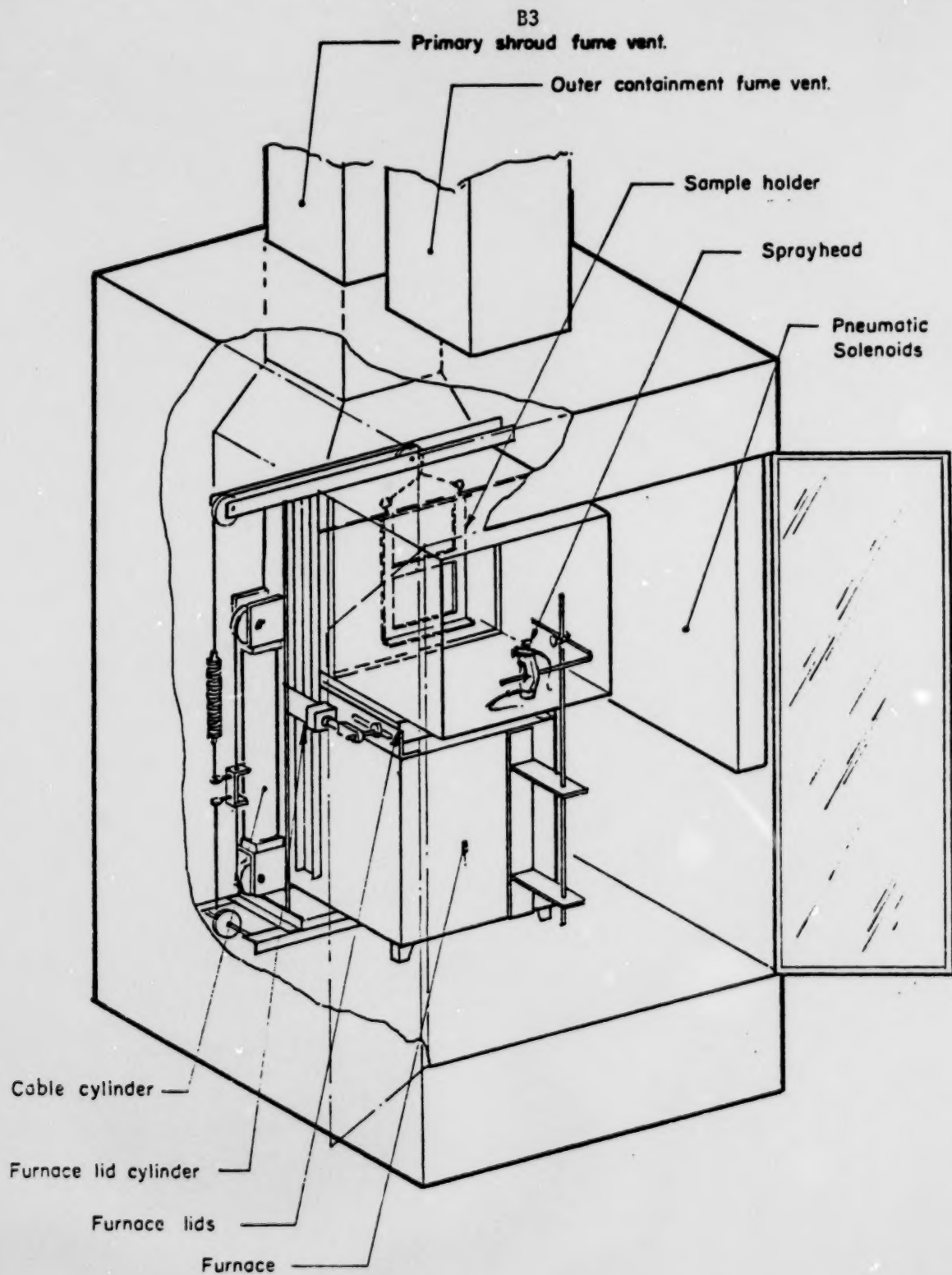


FIGURE B-1 SKETCH OF THE O.R.F SPRAY PYROLYSIS TEST APPARATUS.

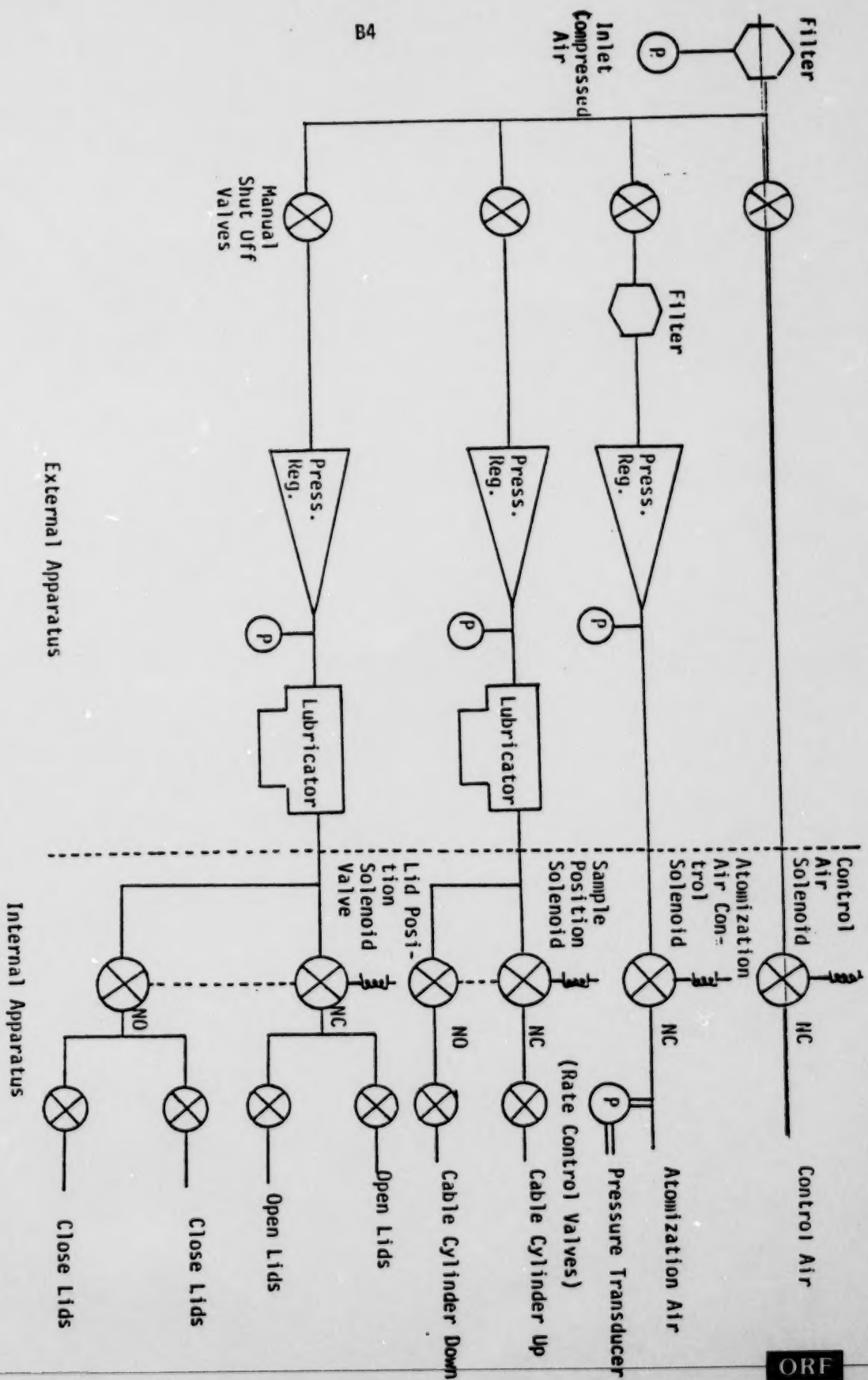


FIGURE B-2: Pneumatic Control Schematic of the ORF Spray Pyrolysis Test Apparatus

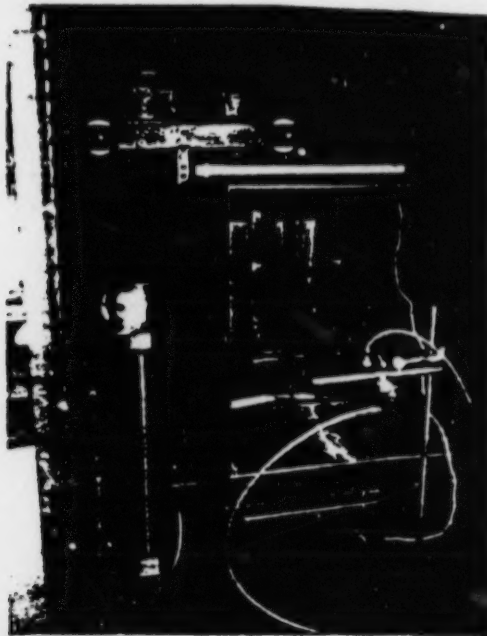
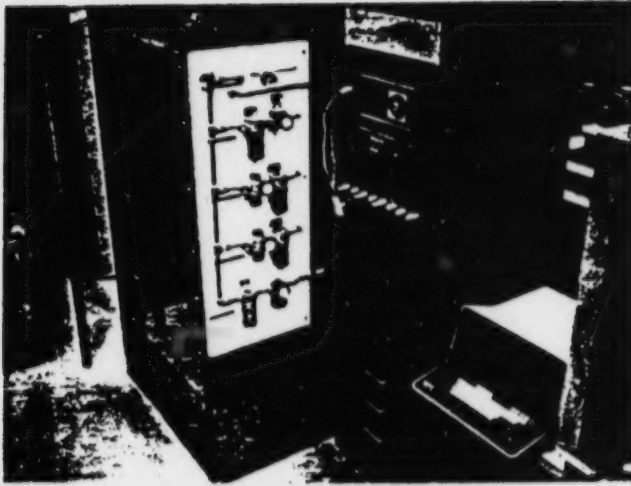


FIGURE B-4: Photographs of the ORF Spray Pyrolysis Test Apparatus

APPENDIX C

Substrate Temperature Profile Study

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APPENDIX B

SPRAY PYROLYSIS TEST FACILITY AT ORF

B-3 Enhanced Capabilities at ORF

The spray pyrolysis development system described in Section B-2 has certain capabilities beyond those currently built in. One of the most important is the possibility of using the system for toxic materials. This modification would involve the use of a recirculating scrubber system on the primary fume shroud (see Figure B-1). This would remove most of the toxic materials and fumes while the negative pressure in the containment booth is maintained by the exhaust system. For highly toxic materials the negative pressure exhaust stream could also be adapted for gas treatments.

The second extension of capability beyond that required by tin oxide is substrate temperature. Tin oxide deposition onto glass substrates requires a furnace temperature of approximately 800°C in order to prevent substrate fracture from thermal shock by means of surface crack heating. The system is capable of using substrate temperatures in excess of 1100°C with minimal modifications.

The third extension of capability is the adaptation of the system for inert atmosphere use. This would require some modifications of the primary fume shroud system in order to operate at a positive pressure while the outer containment operated under negative pressure.

It is believed that the system which exists at ORF is a versatile and powerful tool for the development of spray pyrolysis techniques. In addition, this system would be extremely valuable in the determination, specification and optimization of operating parameters for pilot or production systems. Photographs of the ORF system are presented as Figure B-4.

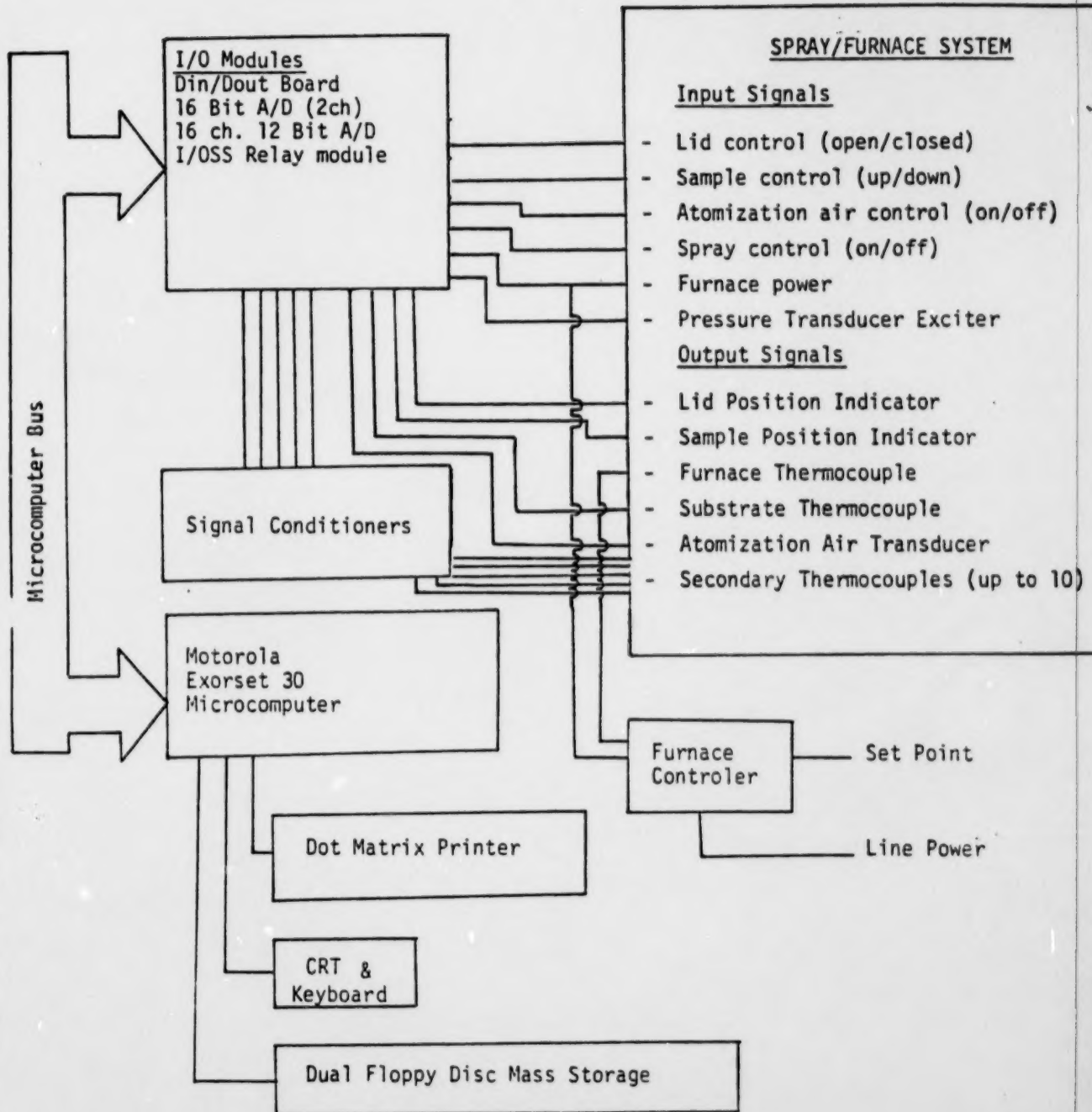


FIGURE B-3: Control and Instrumentation Block Diagram of the ORF Spray Pyrolysis Test Apparatus

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Temperature Profile of Window Glass

Temperature ($^{\circ}\text{C}$) vs Time (minutes, seconds)

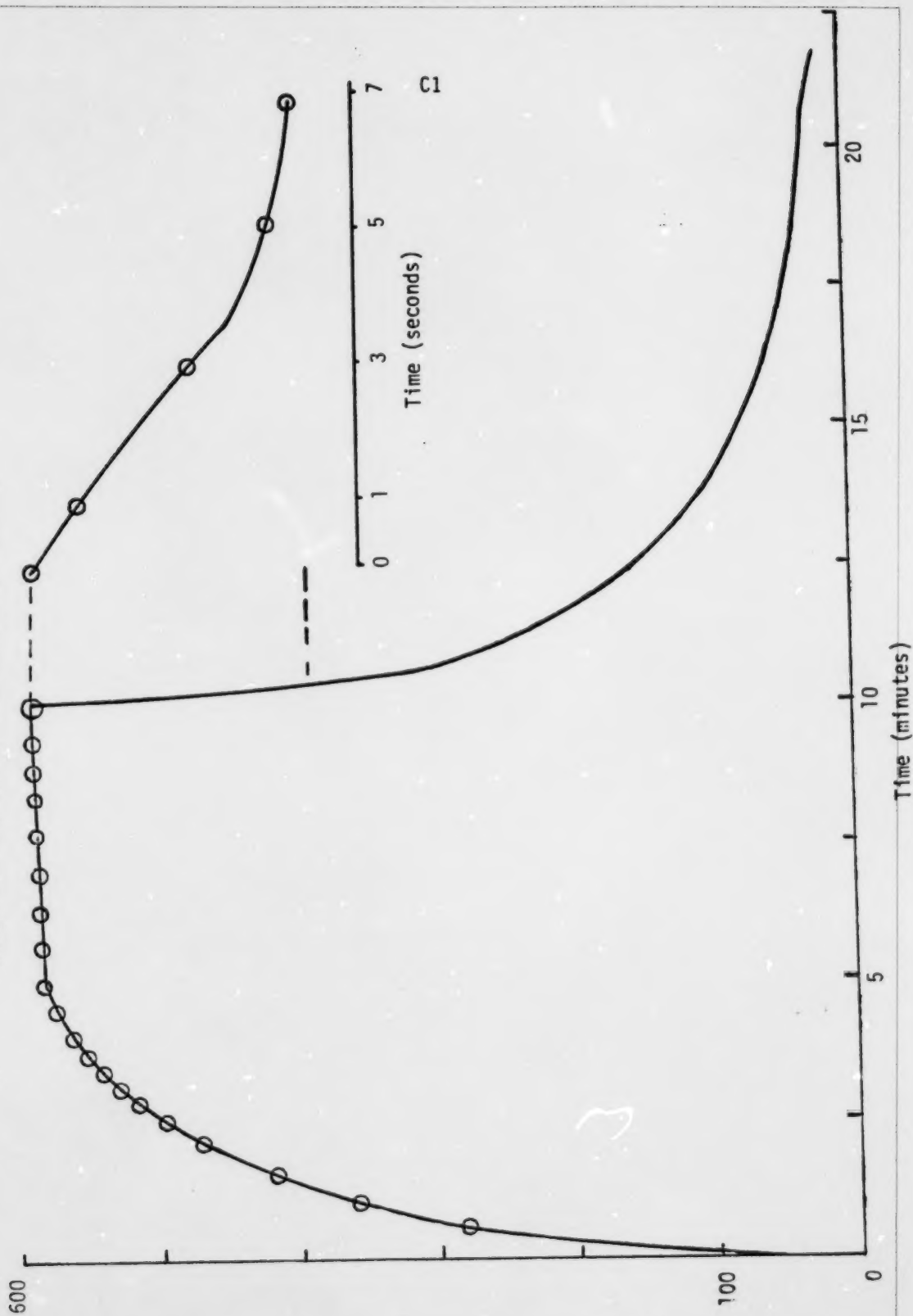
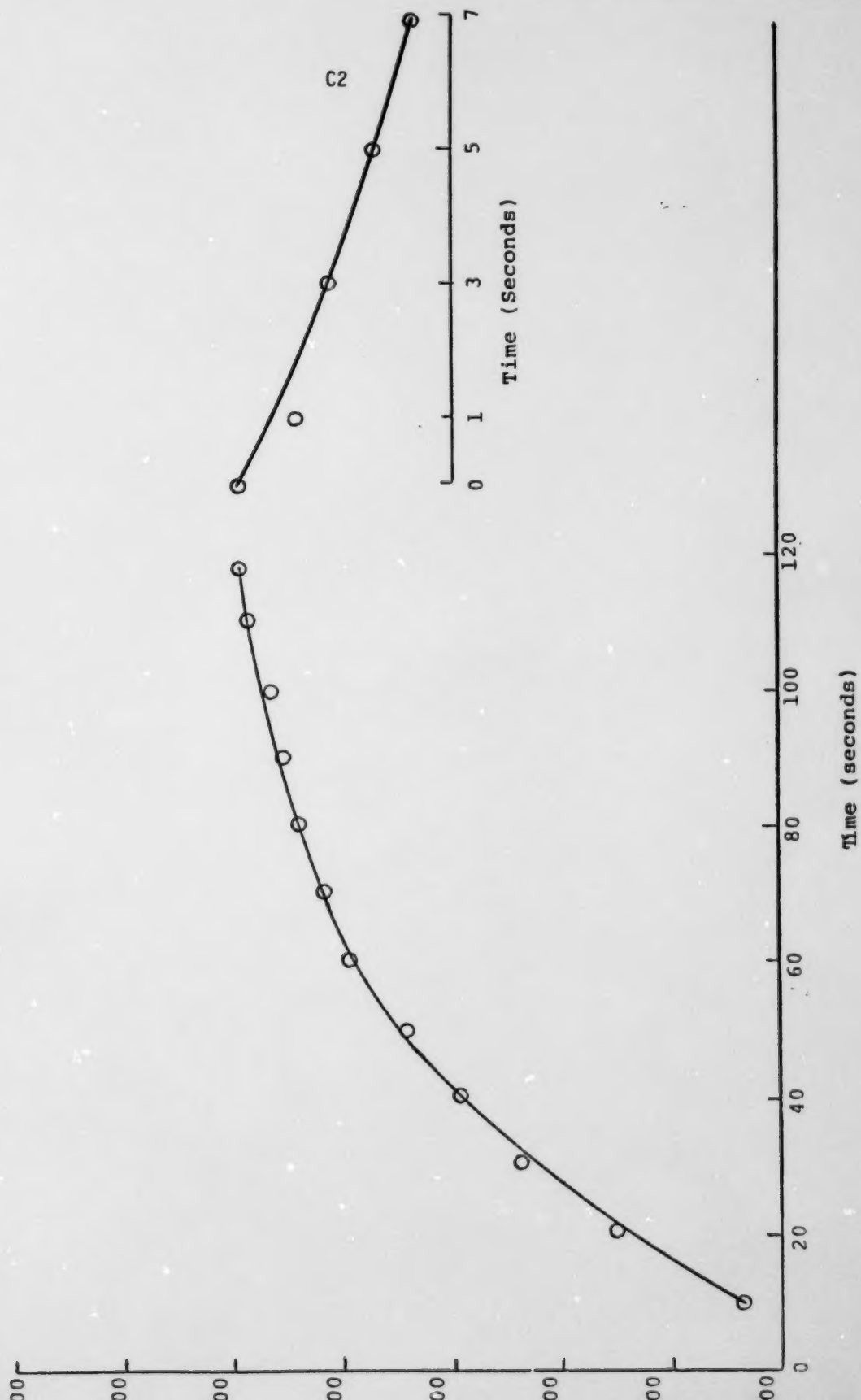


FIGURE C2

Temperature Profile of Window Glass - Temperature ($^{\circ}\text{C}$) vs Time (Seconds)



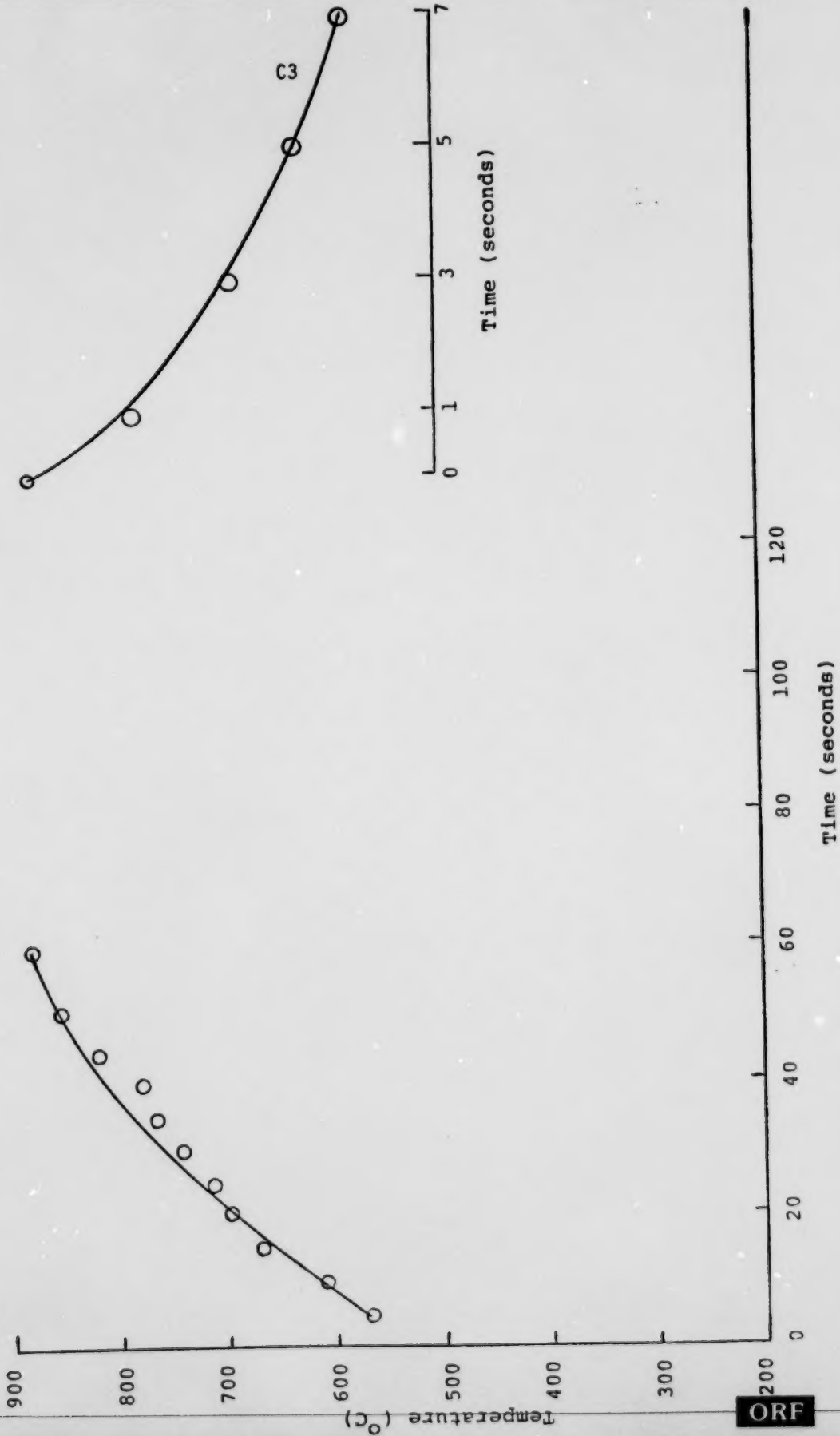


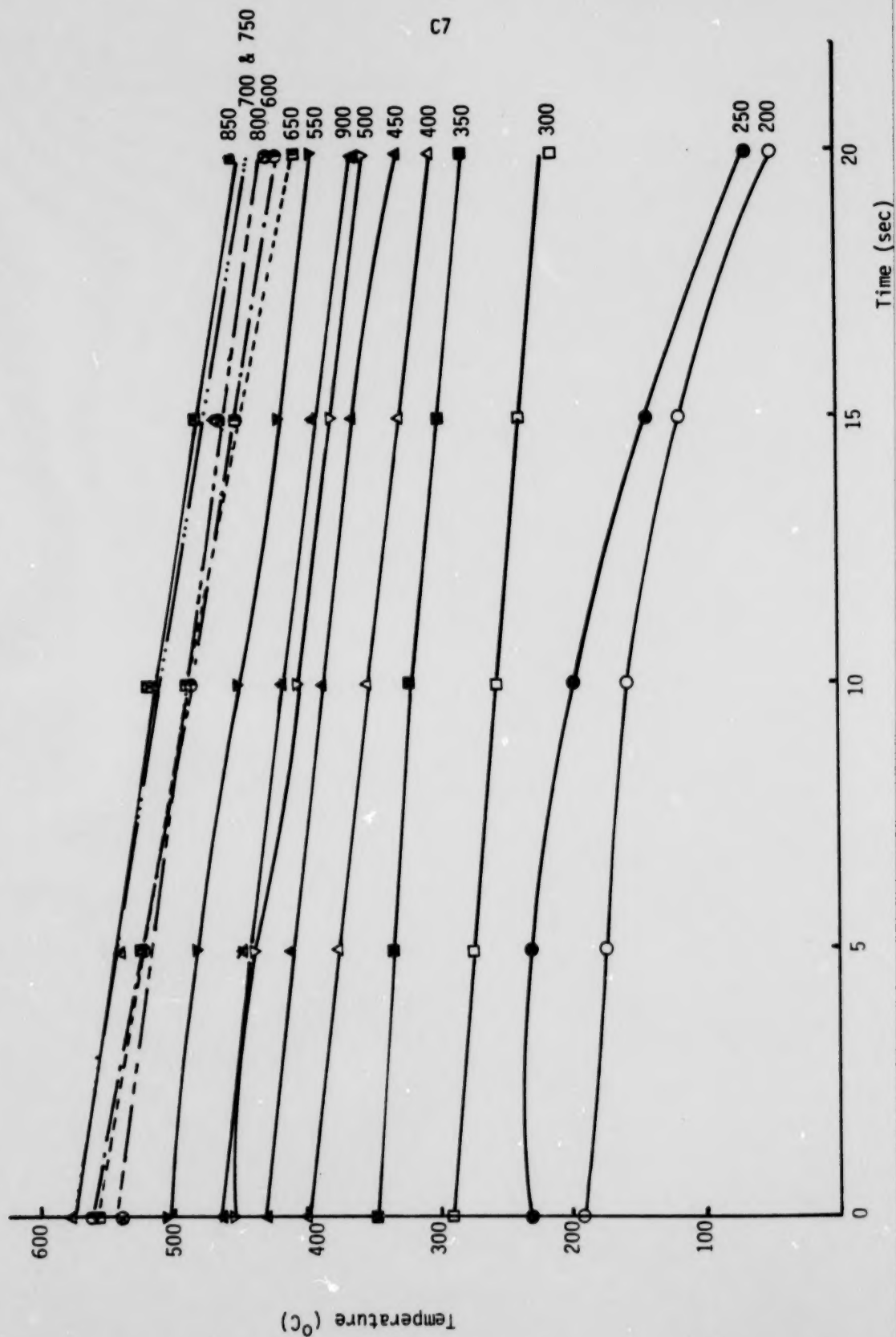
TABLE C1

Window Glass Substrate Temperature Profile
(Unsprayed)

Temperature (°C)	Duration (min.)	Glass Surface Temperature (a)				
		0 *	5s	10s	15s	20s
200	30	217	214	210	206	202
250	30	264	258	253	247	241
300	30	307	302	297	291	285
350	20	353	346	339	333	325
400	8	412	403	396	387	378
450	8	443	434	424	414	406
500	7	492	477	466	452	441
550	6	531	521	506	492	477
600	6	554	543	532	513	499
650	5	574	564	549	532	513
700	4	613	595	574	554	538
750	3	595	582	560	543	527
800	2	543	532	513	499	482
850	2	569	543	513	474	443
900	1	454	443	429	416	375

* seconds

Figure C5: Time vs Temperature Profile of Heat Treated Window Glass
(Sprayed with Etlylalcohol)



APPENDIX D

Results of Spraying Trials

TABLE D1 Spray Parameter Optimization

Plate Number	Air Pressure (psi)	Solution Pressure (psi)	Orifice Size (in)	Distance to Substrate (in)	Spray Cycle (sec)	Comments
67-68	60	70	1/4J-2A	15	10	
69,71,73 75	40	70	1/4J-2A	18	10	
70,72 76,77	40	70	1/4J-2A	18	(3sec spray; 2 sec off)x3	
74	40	70	1/4J-2A	18	3	
78,79 99,100	40	70	1/4J-2A	18	5	
96	40	70	1/4J-2A	18	S*)2, HT**)10, S2	
98,101	40	70	1/4J-2A	18	S5, HT10, S5	
103	40	70	1/4J-2A	18	(S5, HT30)x3	
104	40	70	1/4J-2A	18	S5, HT30, S5	
105	40	70	1/4J-2A	18	S5, HT60, S5	
107,108	40	70	1/4J-2A	18	S5, HT25, S5	
109,111 112	40	70	1/4J-2A	18	S10, HT25, S10	
110	40	70	1/4J-2A	18	S15, HT25, S10	
114	40	70	1/4J-2A	18	S4	

S: Spray Duration

HT: Heat Treatment

TABLE D1 (continued)

Plate Number	Air Pressure (psi)	Solution Pressure (psi)	Orifice Size (in)	Distance to Substrate (in)	Spray Cycle (sec)	Comments
115,122	40	70	1/4J-2A	18	S10	
116	60	70	1/4J-2A	18	S15	
117	60	70	1/4J-2A	18	S15, HT25, S15	
118,121 123,125	40	70	1/4J-2A	18	S5	
119	40	70	1/4J-2A	18	S5, HT90, S5	
120	40	70	1/4J-2A	18	S5, HT90, S5	
124	40	70	1/4J-2A	18	S5, HT45, S5	
128	40	70	1/4J-2A	18	S10, HT60, S10	
129,130 133,135	40	70	1/4J-2A	18	S10, HT90, S10	
132	40	70	1/4J-2A	18	S10, HT120, S10	
134	40	70	1/4J-2A	18	S10, HT90, S10	
136,137 138	40	70	1/4J-2A	18	(1) S10, HT90, S10 (2) S10	
142,143 154,165	40	70	1/4J-2A	18	S10, HT90, S10	
145,147 162	40	70	1/4J-2A	18	S10	

TABLE D1 (continued)

Plate Number	Air Pressure (psi)	Solution Pressure (psi)	Orifice Size (in)	Distance to Substrate (in)	Spray Cycle (sec)	Comments
146, 148 149, 152 153, 163 164	40	70	1/4J-2A	18	S10, HT300, S10	
151	40	70	1/4J-2A	18	S10, HT300	
167-199	40	70	1/4J-2A	18	S10	
200-204, 241, 224- 227, 233	65	70	1/4J-2A	18	S10	
205-223 234-235 237-244 228, 229	65	70	1/4J-2A	18	S20	
69	40	70	1/4J-2A	18	S10	
118	40	70	1/4J-2A	18	S5	
152	40	70	1/4J-2A	18	S10, HT300, S10	
172-193	40	70	1/4J-2A	18	S10	
163	40	70	1/4J-2A	18	S10, HT300, S10	
228, 229 237	40	70	1/4J-2A	18	S20	
147	40	70	1/4J-2A	18	S10	

TABLE D1 (continued)

Plate Number	Air Pressure (psi)	Solution Pressure (psi)	Orifice Size (in)	Distance to Substrate (in)	Spray Cycle (sec)	Comments
242, 259 246	40	70	1/4J-2A	18	S20	
247-252	40	70	1/4J-2A	18	S10	
253-257	40	70	1/4J-2A	18	S10	
258	40	70	1/4J-2A	18	S15	
246, 259 260	65	70	1/4	18	20	Single coat.
247-257	65	70	1/4	18	10	Single coat.
258	65	70	1/4	18	5	Single coat.
263	65	70	1/4	18	S10, HT300, S10 HT300, S5	3 coats.
264	65	70	1/4	18	HT5, S30	Shattered
265	65	70	1/4	18	HT45, S5, HT45, S5	Cracked.
266	65	70	1/4	18	HT15, S3, HT15, S5.	

TABLE D7 (continued)

Plate #	Spray Cycle	Solvent	Concent-ration	pH	Mix Ratio	Furnace Temp (°C)	Heating Duration (min)	Results/Remarks			
								X-Ray	S. E. M	Hardness	Abrasion
Al Isopropoxide (continued)	259	Toluene	20 wt%			300	10				Very fine white powder Heat Treated 850°C 2 min.
260		Toluene	20 wt%			300	10				Very fine white powder.
Al Sec-Butoxide											
149		Propanol	20 wt%	100%		200	12				White loose powder.
Al (OCH(CH ₃) ₂) ₃ in Toluene											
112		Toluene	20 wt%			850	2				
299	1x5s	Toluene	20%			650	6				Fair to good adhesion. White basis slightly powdery, light col. rings.
300	1x30s	Toluene	20%			450	8				Fair adhesion White powdery finish.
301	1x10s	Toluene	20%			350	6				Fair adhesion very light base

* Sprayed once for 5 sec.

ORF

TABLE D2

SnCl₄·5H₂O

Plate #	Spray Cycle	Solvent	Concentration	pH	Mix Ratio	Furnace Temp (°C)	Heating Duration (min)	Results/Remarks				
								X-Ray	S.E.M	Hardness	Abrasion	Appearance
1	5x1*	H ₂ O	0.2M	-	-	500	5				White powder	
2	10x1	H ₂ O	0.2M	-	-	550	5				White powder	
3	10x1	H ₂ O	0.2M	-	-	600	5				White powder	
4	10x1	50% Ethanol 50% H ₂ O	0.4M	-	-	625	5				Good	
5	10x2		0.4M	-	-	625	5				Good	
6	10x1		0.4M	-	-	625	5				Good	
7	10x1		0.4M	0.4	-	625	5				Good	
8	10x1		0.4M	0.4	-	625	5				Good	
9												
10	10x1		0.4M	0.4	-	650	5	Discarded			Thick powdery White powder	
11	10x1		0.4M	0.4	-	625	5					
12	10x1		0.4M	0.4	-	625	5	Discarded				
13								Discarded				
14												
15	10x1		0.2M	0.6	-	800	3				Good	
16	10x1		0.2M	0.6	-	800	3				Good	
17	10x1		0.4M	0.4	-	800	3				Good	
18	10x1		0.8M	0.4	-	900	3				Dull	

* Sprayed once for 5 sec.

D5

TABLE D2 (continued)

Plate #	Spray Cycle	Solvent	Concentration	pH	Mix Ratio	Furnace Temp (°C)	Heating Duration (min)	Results/Remarks				
								X-Ray	S.E.M	Hardness	Abrasion	Appearance
19	10x1	50% Ethanol 50% H ₂ O	0.8M	0.4	-	900	2				Dull	
20	10x1		0.8M	0.4	-	900	1				Cracked	
21	10x1		0.8M	0.4	-	900	1				Dull	
22	10x1		0.8M	0.4	-	950	2				Cracked	
23	10x1		0.8M	0.4	-	950	1				Cracked before spraying	
24	10x1		0.8M	0.4	-	1000	1				"	
25	10x1	50% Ethanol 50% H ₂ O	0.8M	0.4	-	1000	1/2				"	
26	10x1		0.8M	0.4	-	900	1					
27	10x1											
28	10x1		0.8M	0.4	-	850	2				Good	
29	10x1		0.8M	0.4	-	850	2				Good	
30	10x1		0.8M	0.4	-	850	2				Good	
31	10x1	50% Ethanol 50% H ₂ O										
32	10x1		0.8M	0.4	-	850	2				Good	
33	10x1		0.8M	0.4	-	900	1/2				Crack before spraying	
34	10x1		0.8M	0.4	-	900	1/2				Spraying	
40	10x1		60 wt%	0.2	-	850	2				Good	
41	10x1		60 wt%	0.2	-	850	2				Good	
42	10x1	50% Ethanol 50% H ₂ O	60 wt%	0.2	-	625	5				Cracked	
43	10x1		60 wt%	0.2	-	625	5				Gritty	

* Sprayed once for 5 sec.

ORF

D20

Plate #	Spray Cycle	Solvent	Concent-ration	pH	Mix Ratio	Furnace Temp (°C)	Heating Duration (min)	Results/Remarks			
								X-Ray	S.E.M	Hardness	Abrasion
302	1x60s	Toluene	20%			350	6				Fair adhesion white opaque.
303	1x10s	Toluene	20%			650	6				No coating.
304	1x30s	Toluene	20%			650	6				Poor adhesion light dust covering surface.
305	5x2s 2s hold	Toluene	20%			650	6				Fair adhesion.
306A	3x10s	Toluene	20%			700					Poor adhesion.
307	1x10s		20%			500	6				Poor adhesion light white dust.
308	1x10s					400	8				Poor adhesion Light white dust.
309	1x10s					550	6				Poor adhesion.
310	1x2s 2 hold					350	7				Fair adhesion white, light powder on surface.
311						450	7				Fair adhesion white, light powder.

* Sprayed once for 5 sec.

ORF

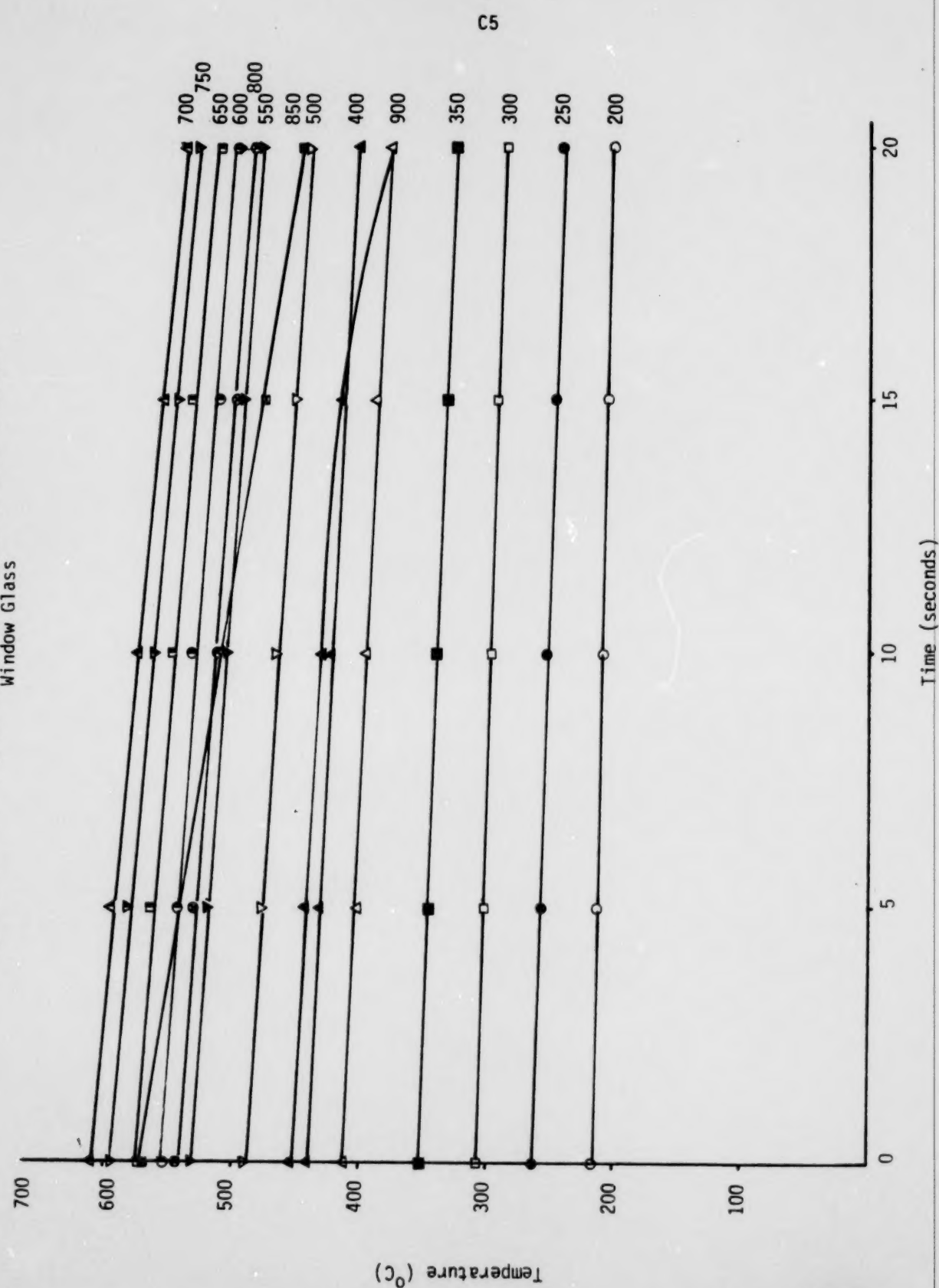
TABLE D4 (continued)

Plate #	Spray Cycle	Solvent	Concentration	pH	Mix Ratio	Furnace Temp (°C)	Heating Duration (min)	Results/Remarks			
								X-Ray	S.E.M	Hardness	Abrasion
232		Toluene	20 wt %	<0		800	1 3/4				
238		Toluene	20 wt %	<0		200	12				Transparent
340	1x5s	Freon	-	-	-	400	8/4**				Some difficulty in spraying
341	1x12s	Benzene				400	8/4				Comments: Spray plugged instantaneously. Discarded.
342	2x12s	CCl ₄				400	8/4				Very thin powder. No adherence.
343	1x12s	Chloroform				400	8/4				Spotty coating. Good adherence.
344	1x12s	Toluene				400	3/4				White powder. No adherence.
345	1x12s	Toluene				650	5/4				White powder. No adherence.
345	1x12s	Chloroform				650	5/4				No visible coating.
347	1x12s	CCl ₄				650	5/4				White powder. No adherence.
349	1x12s	Benzene				650	5/4				Traces of white deposit. No adherence.
350	1x12s	Toluene				650	5/4				White dust. No adherence.
											Sprayed w N ₂ as vehicle. White powder. No adherence.

** 4 min. final heat treatment after last application.

* Sprayed once for 5 sec.

Figure C4: Time vs Temperature (Unsprayed) of Heat Treated Window Glass



ORF

C6

TABLE C2

Window Glass Substrate Temperature Profile
(Sprayed with Ethylalcohol)

Furnace Condition		Glass Surface Temperature (a)				
Temperature (°C)	Duration (min.)	0s*	5s	10s	15s	20s
200	30	194	174	160	122	52
250	30	238	231	199	129	81
300	30	294	277	258	235	217
350	20	348	335	320	300	283
400	8	400	377	352	330	307
450	8	431	414	388	366	332
500	7	459	441	410	383	359
550	6	509	486	452	421	398
600	6	563	522	488	454	424
650	5	560	532	491	454	416
700	4	582	543	513	474	454
750	3	582	549	513	474	454
800	2	542	532	497	466	434
850	2	581	543	520	482	454
900	1	468	449	418	393	366

* seconds

ORF

TABLE D5

Al(NO₃)₃·9H₂O

Plate #	Spray Cycle	Solvent	Concentration	pH	Mix Ratio	Furnace Temp (°C)	Heating Duration (min)	Results/Remarks			
								X-Ray	S.E.M	Hardness	Abrasion
107		HO ⁵ H ² CO ² H	20 wt %	1.4	50/50	850	20				
108			20 wt %	1.4	50/50	850	20				
109			20 wt %	1.4	50/50	850	20				
110			20 wt %	1.4	50/50	850	20				
111			30 wt %	<0	50/50	850	20				
118			20 wt %	1.4	50/50	400	8				
119			20 wt %	1.4	50/50	400	8				
120						400	10				
121						400	6				
122						400	8				
123						650	5				
124						650	5				

* Sprayed once for 5 sec.

ORF

TABLE D2 (continued)

Plate #	Spray Cycle	Solvent	Concentration	pH	Mix Ratio	Furnace Temp (°C)	Heating Duration (min)	Results/Remarks				
								X-Ray	S.E.M	Hardness	Abrasion	Appearance
49	10x1	50% Ethanol 50% H ₂ O	0.8M	0.4	-	850	2				Fair	
50	10x1		0.8M	0.4	-	850	2				Good	
57	10x1											
58												
59												
60	10x1	C ₂ H ₅ OH H ₂ O	0.8M	0.4	-	850	2				Good	
61	10x1		0.8M	0.4	-	850	2				Good	
62			.4M	.4	50/50	625	5			N/A	Good	
69		H ₂ O/HCl	11.5M	<0	3/1	850	2			876 KHN	Good	
70		H ₂ O/HCl	11.5M	<0	3/1	850	2			N/A	Good, but spotty in areas	
157		H ₂ O/HCl	50uf% wt%		3:2	Deformed					Even transparent rain-bow like	
158						"						
159						"						
160						"						
161						"						
167						850	2					

* Sprayed once for 5 sec.

TABLE D2 (continued)

Plate #	Spray Cycle	Solvent	Concent-ration	pH	Mix Ratio	Furnace Temp (°C)	Heating Duration (min)	Results/Remarks				
								X-Ray	S.E.M	Hardness	Abrasion	Appear-ance
175		H ₂ O/HCl	50uf%wt%		3:2	600	5½					
176		H ₂ O/HCl	50uf%wt%		3:2	600	5½					
184		H ₂ O/HCl	50uf%wt%		3:2	650	5					
197		H ₂ O/HCl	50uf%wt%		3:2	700	4					
198		H ₂ O/HCl	50uf%wt%		3:2	750	3					

D8

* Sprayed once for 5 sec.

TABLE D3

 $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$

Plate #	Spray Cycle	Solvent	Concent-ration	pH	Mix Ratio	Furnace Temp (°C)	Heating Duration (min)	Results/Remarks				
								X-Ray	S.E.M	Hardness	Abrasion	Appear-ance
142		H ₂ O/ C ₂ H ₅ OH	.8M	1.7	50/50	400	8					Grey powder centre, white outer area.
147						200	12					Flaky areas white
143						200	12					Bright white areas of good adhesion.

D9

* Sprayed once for 5 sec.

TABLE D4

AlCl₃ (Anhydrous)

Plate #	Spray Cycle	Solvent	Concent-ration	pH	Mix Ratio	Furnace Temp (°C)	Heating Duration (min)	Results/Remarks				
								X-Ray	S.E.M	Hardness	Abrasion	Appearance
162		C ₂ H ₅ OH	20 wt %	<0		300	10				Pale yellow loose powder	
163						250	11				Loose beige powder	
164						200	12				Thick layer of loose white powder	
165						400	8				Light covering of white powder	
166						650	5				Sparse, white powder covering	
231		Toluene	20 wt %			850	2				Fine powder	

* Sprayed once for 5 sec.

D10

TABLE D5 (continued)

Plate #	Spray Cycle	Solvent	Concentration	pH	Mix Ratio	Furnace Temp (°C)	Heating Duration (min)	Results/Remarks				
								X-Ray	S.E.M	Hardness	Abrasion	Appearance
125		$\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH}$	20 wt %	1.4	50/50	500	6					Powder surface some thin adhesive under -coat.
126						450	7					Thin
127						450	6					Thin
128						450	6					Thick but not even.
129						400	8					Very good, even
130						400	8					Non-coated centre, evenness elsewhere.
131						400	8					Uneven white
132						350	9					Uneven white
133		100 % ethanol			100 %	400	8					White powder
134					100 %	400	8					White powder
135					100 %	400	8					White powder
143		$\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH}$	20 wt %	1.4	50/50	400	8					Rough white, even coating
												HEAT TREAT 850°C - 2 min.
145						200	12					Thin, white sticky centre.
												HEAT TREAT 850°C - 2 min.

* Sprayed once for 5 sec.

TABLE D5 (continued)

Plate #	Spray Cycle	Solvent	Concentration	pH	Mix Ratio	Furnace Temp (°C)	Heating Duration (min)	Results/Remarks				
								X-Ray	S.E.M	Hardness	Abrasion	Appearance
146		H ₂ O/ C ₂ H ₅ OH	20 wt%	1.4	50/50	200	12					Thick white improved adhesive due to heat.
151						200	12					Bore centre, white powder
152						200	12					HEAT TREAT 850°C - 2 min. Even white coating.

TABLE D6

 $Al_2(SO_4)_3 \cdot 16H_2O$

Plate #	Spray Cycle	Solvent	Concent-ration	pH	Mix Ratio	Furnace Temp (°C)	Heating Duration (min)	Results/Remarks				
								X-Ray	S.E.M	Hardness	Abrasion	Appearance
228		H ₂ O	20 wt%		2.2	600	6				White powder	
229						700	4				Even heavy layer powder	
230						800	2				White powder	
237						200	12				Even white	
240						250	11				Even white	
246						200	12				Smoked appearance HEAT TREATMENT	
247											Temp. 500 Time 8	
											Clear coating in centre white adhesive edges HEAT TREATMENT	
248											Temp. 650 Time 6	
											"	
											Temp. 850 Time 2	
249											"	
											Temp. 1000 Time 1.1/3	
250						Discarded						

* Sprayed once for 5 sec.

TABLE D6 (continued)

Plate #	Spray Cycle	Solvent	Concentration	pH	Mix Ratio	Furnace Temp (°C)	Heating Duration (min)	Results/Remarks			
								X-Ray	S.E.M	Hardness	Abrasion
251		H ₂ O	20 wt%		2:2	200	12				
252		"	"		"	"	"				
253		"	"			250	11				
254		"	"			"	"				
255		"	"			"	"				
256		"	"			"	"				
257		"	"			"	"				
258		"	"			"	"				
263		"	"		2.2	350	9				
264		"	"		2.2	900	0.5				
Even, thin white coating Clear centre coating. HEAT TREATMENT Temp. 500 Time 8 HEAT TREATMENT Temp. 650°C Time 6 HEAT TREATMENT Temp. 850°C Time 2 min. HEAT TREATMENT Temp. 1000°C Time 1½ Poor adhesion. N/A. Flaky white top adhesive undercoat. N/A. Glass shattered on impact of spray.											

TABLE D6 (continued)

Plate #	Spray Cycle	Solvent	Concentration	pH	Mix Ratio	Furnace Temp (°C)	Heating Duration (min)	Results/Remarks				
								X-Ray	S.E.M	Hardness	Abrasion	Appearance
265		H ₂ O	20 wt%	2.2		900	45s					N/A
266		"	"	2.2		900	15s					N/A

D17

* Sprayed once for 5 sec.

TABLE D7

Al. Alkoxide

Plate #	Spray Cycle	Solvent	Concent-ration	pH	Mix Ratio	Furnace Temp (°C)	Heating Duration (min)	Results/Remarks				
								X-Ray	S.E.M	Hardness	Abrasion	Appearance
Al Isopropoxide												
153		Benzene	20 wt%			200	12					Loose white powder. Powdery surface. Some more adhesive large below.
154		Benzene	20 wt%			400	8					Thin film white powder
155		Benzene	20 wt%			850	2					Thin small amount of powder.
156		Benzene	20 wt%			650	5					Powder formed before reach- ing substrate.
220		Toluene	20 wt%			200	12					Sputtering effect white powder dots.
221		Toluene	20 wt%			200	12					Thin uneven white.
236		Toluene	20 wt%			400	8					Thin white.
241		Toluene	20 wt%			250	11					Thin even white coat.
242		Toluene	20 wt%			300	10					White
243		Toluene	20 wt%			350	9					Fine white powder.
244		Toluene	20 wt%			400	8					

* Sprayed once for 5 sec.

TABLE D12

Samples sprayed w. n-Butylzirconate - Single coat.

Plate #	Spray Cycle	Furnace Temp.	Heating Duration (min)		Comments	Results		
			Initial	Between Coats		X-Ray	S.E.M.	Abrasion
356	1x10s	400	8	-	Very thick. Poor adherence.	amorphous " " Start of T&C. Start of T&C. Some T&C. " Thin. Barely visible. Thin.		
357	1x10s	450	8	-	No flaking. Refl. good adherence. Fingernail: scratch.			
358	1x10s	500	8	-	Coating a bit thin.			
359	1x10s	550	7	-	Very thin.			
361	1x10s	600	7	-	Bit thicker.			
362	1x10s	650	5	-	Very thin.			
363	1x10s	700	4	-	Thick, Powdery. No adherence.			
364	1x10s	750	3	-	Thin.			
365	1x10s	650	5	-	Barely visible.			
366 367 368	1x10s	650	5	-	Thin.			

T = Tetragonal
C = Cubic

D21

TABLE D7 (continued)

Plate #	Spray Cycle	Solvent	Concentration	pH	Mix Ratio	Furnace Temp (°C)	Heating Duration (min)	Results/Remarks		
								X-Ray	S.E.M.	Abrasion
312	5x5s 2s hold	Toluene	20%			800	3			Poor adhesion white dust covering surface.
313						800	3.5			Fair adhesion white, powdery surface.
314						800	3			Poor adhesion white dust covering surface.
Butanol 100%										
315)						500	6			Clear.
316)										Clear.

* Sprayed once for 5 sec.

ORF

TABLE D13

Samples sprayed w. n-Butylzirconate - Multi-coat.

Plate #	Spray Cycle	Furnace Temp. °C	Heating Duration (min)		Comments	Results		
			Initial	Between Coats		X-Ray	S.E.M.	Abrasion
332	5x10s	500	8	5	Powdery in centre.	D36		
333	5x5s 1x2s	550	7	4	No cracks in coating.			
334	5x5s	600	6	4	Sample broke.			
335	5x5s	450	10	8	Powdery residue. Uneven coating.			
336	5x5s	500	8	5	Fair.			
337	5x5s	600	7	5	Fair.			
338	5x5s	650	6	4	Warped. Cracks in coating.			
339	5x5s	400	8	6	Powdery, thick in centre.			
350	5x5s	700	4	2	Thin.			
351	5x5s	750	3	2	Sample broke and dropped in the furnace - discarded.			
360	5x5s	800	2	2	Warped. Coating opaque and plicated.			
354	5x5s	650	5	4	Cracks in coating.			
355	5x5s	700	4	2	Very thin.			
370	5x5s	700	4	2	Cracks in coating.			
371	5x5s	750	3	1	Very thin.			
372	5x5s	800	2	2	No cracks.			

TABLE D8

SnCl₄·5H₂O/AlCl₃·6H₂O

Plate #	Spray Cycle	Solvent	Concentration	pH	Mix Ratio	Furnace Temp (°C)	Heating Duration (min)	Results/Remarks		
								X-Ray	S.E.M.	Abrasion
51	10x1		7.5 wt% 7.5 wt%	0.3		850	2			Powdery
52			9 wt% 6 wt%	0.35		850	3			Powdery uneven
53			9 wt% 6 wt%			850	3			Powdery areas.
54			12 wt% 3 wt%	0.4		850	3			Best but vague.
55			9 wt% 6 wt%	0.6		850	3			Powdery.
56			12 wt% 3 wt%	0.5		850	3			Powder.
63			13.5 wt% 1.5 wt%	.6	50/50	625	5			Weak colour.
64			12 wt% 3 wt%	.4	50/50	625	5			Glass cracked spray nozzle out of position.
65			12 wt% 3 wt%	.4	50/50	625	5			Broke after spray white powder.
66			10.5 wt% 4.5 wt%	.4	50/50	625	5			Broke white powder.

* Sprayed once for 5 sec.

ORF

TABLE D13 (continued)

Plate #	Spray Cycle	Furnace Temp. °C	Heating Duration (min)		Comments	Results			
			Initial	Between Coats	Final	X-Ray	S.E.M.	Hardness	Abrasion
373	5x5s	750	3	2	2	Thick, cracks. Sample was heat treated in isothermal furnace 760°C/2 min - cracks remained.			
375	5x5s	400	8	6	6	Brownish deposit in centre, whole in surrounding area. Poor adherence.			
376	5x5s	450	7	5	5	Good coating, good adherence.			
377	5x5s	500	6	4	4	Thin, good adherence.			
378	5x5s	550	6	4	4	Barely visible. No cracks.			
379	5x5s	550	6	4	4	Barely visible.			
380	5x5s	600	6	4	4	Liq cap 2850ss - V. Thin.			
381	5x5s	550	6	4	4	Liq cap 2850ss - more visible.			
382	5x10s	550	6	4	4	Liq cap 2850ss - good coat.			
383	5x15s	550	6	4	4	Thinner. Shattered.			
384	5x15s	550	6	4	4	Liq cap 2050ss - thin.			
385	5x5s	550	6	4	4	Same			
386	5x5s	550	6	4	4	Spray blocked. Discarded.			
387	5x10s	550	6	4	4	Very thin.			
388	5x10s	550	6	4	4	Thin - scrapped.			
389	5x15s	550	6	4	4				

ORF

D37

TABLE D8 (continued)

Plate #	Spray Cycle	Solvent	Concentration	pH	Mix Ratio	Furnace Temp (°C)	Heating Duration (min)	Results/Remarks			
								X-Ray	S.E.M	Hardness (KHN)	Abrasion
67			9.0 wt% 6.0 wt%	.4	50/50	625	5				Cracked heavy white powder.
68		50% ethanol 50% H ₂ O	7.5 wt% 7.5 wt%	.30	50/50	625	5				Broke, heavy white powder.
71		H ₂ O/HCl	70 wt% 10 wt%	<0	3/1	850	2			735	SnO ₂ coating with loosely attached aluminum.
72		"	"	"	"	850	2			N/A	SnO ₂ coating white powdered centre.
73		"	60 wt% 20 wt%	"	"	850	2			838	Powdery.
74		"	"	"	"	850	2			N/A	Powdery.
77		"	75 wt% 5 wt%	"	"	850	2			807	Powdery but even.
78		"	"	"	"	850	2			N/A	Good but sputtering problem.
95		"	"	"	"	850	2			N/A	Sputtering problem.
96		"	"	"	"	850	2			N/A	Sputtering uneven.

* Sprayed once for 5 sec.

ORF

D23

TABLE D14

n-Butylzirconate - 550°C

Plate #	Spray Cycle	Furnace Temp. °C	Heating Duration (min)		Comments	Results			
			Initial	Between Coats	Final	X-Ray	S.E.M.	Hardness	Abrasion
378'	1x10s	550	6	-	-	Very thin.			
379'	T = Tetragonal c = cubic.								
380'									
381'		550	6	-	-	Very thin.			
382'		550	6	-	-	Shattered - discarded.			
383'	1x10s	550	6	-	-	Very thin.			
384'	2x10s	550	6	4	4	Thin.			
385'	2x10s	550	6	4	4	Thin.			
386'		550	6			No coating.			
387'		550	6			No coating.			
388'		550	6			No coating.			

ORF

D39

TABLE D8 (continued)

Plate #	Spray Cycle	Solvent	Concentration	pH	Mix Ratio	Furnace Temp (°C)	Heating Duration (min)	Results/Remarks			
								X-Ray	S.E.M	Hardness (KHN)	Abrasion
97		H ₂ O/HCl	75 wt% 5 wt%	<0	3/1	850	2				Little powder on surface even coating.
98		"	70 wt% 10 wt%	"	"	850	2			889	Good.
99		"	"	"	"	850	2			868	White adherent powder.
100		"	60 wt% 20 wt%	"	"	850	2			728	Powdered surface.
101		"	"	"	"	850	2			773	
103		"	"	"	"	850	2			791	Good.
104		"	70 wt% 10 wt%	"	"	850	2			945	Good, deformation at edges.
105		"	"	"	"	850	2			N/A	Severe deformation.
174		"	20 wt% 30 wt%	"	3:2	850	2				
183		"	"	"	"	600	5½				
190		"	"	"	"	650	5				
191		"	"	"	"	700	4				

* Sprayed once for 5 sec.

ORF

D24

TABLE D8 (continued)

Plate #	Spray Cycle	Solvent	Concentration	pH	Mix Ratio	Furnace Temp (°C)	Heating Duration (min)	Results/Remarks			
								X-Ray	S.E.M	Hardness	Abrasion
173		H ₂ O/HCl	25 wt%		3:2	850	2				
182		"	25 wt%		"	600	5½				SnO ₂ undercoat flaky white top layer.
189		"	"		"	650	5				
192		"	"		"	700	4				
172		H ₂ O/HCl	30wt% 20 wt%		3:2	850	2				SnO ₂ appears large amount white flakes.
181		"	"		"	600	5½				
188		"	"		"	650	5				
193		"	"		"	700	4				
171		H ₂ O/HCl	35 wt% 15 wt%		3:2	850	2				SnO ₂ appears loose white powder on top.
180		"	"		"	600	5½				
187		"	"		"	650	5				
194		"	"		"	700	4				
170		H ₂ O/HCl	40 wt% 10 wt%		3:2	850	2				SnO ₂ appears small amount white powder.
179		"	"		"	600	5½				
186		"	"		"	650	5				
195		"	"		"	700	4				

ORF

* Sprayed once for 5 sec.

D25

D26

TABLE D8 (continued)

Plate #	Spray Cycle	Solvent	Concentration	pH	Mix Ratio	Furnace Temp (°C)	Heating Duration (min)	Results/Remarks			
								X-Ray	S.E.M	Hardness	Abrasion
168		H ₂ O/HCl	45 wt% 5 wt%		3:2	850	2				
177		"	"		"	600	5½				
178		"	"		"	600	5½				
185		"	"		"	650	5				
196		"	"		"	700	4				
199		"	"		"	750	3				
348	1x8s	Abs C ₂ H ₅ OH				650	5/4				

ORF

Comments
Good coating. Spotty in the center. Some powder with poor adherence. Did abrasion test on a small specimen.

* Sprayed once for 5 sec.

TABLE D13 (continued)

Plate #	Spray Cycle	Furnace Temp.	Heating Duration (min)		Comments	Results			
			Initial	Between Coats		X-Ray	S.E.M.	Hardness	Abrasion
390	5x15s	550	6	4	Afterwards heat treated in isothermal furnace 850°C/1 min.	Amorphous			
438	5x10s	700	4	1	White powder at centre of spray pattern and cracks. Poor adhesion.				
439	5x10s	700	4	1					
440	10x10s	700	4	1	White powder at centre of spray pattern. Fingernail test: scratched.				
441	10x10s	700	4	1					
442	20x10s	700	4	1	Very thick white coating. Fingernail test: scratched.				
443	20x10s	700	4	1					

D38

TABLE D15

N-Butyl-zirconate 700°C

Plate #	Spray Cycle	Furnace Temp. °C	Heating Duration (min)		Comments	Results			
			Initial	Between Coats		X-Ray	S.E.M.	Hardness	Abrasion
413		700	4		No coating.				
414		700	4		No coating.				
415		700	4		No coating.				
416	1x10s	700	4	-	Good appearance but thin hazy looking, few bubbles.				
417	1x10s	700	4	-	No cracks.	Little T+C			
418	1x10s	700	4	-	"	"			
419	1x10s	700	4	2	Small cracks, starting from inclusions. #419 displayed dendritic structure.	Some T+C			
420	1x10s	700	4	2					
421	1x10s	700	4	2					
422	2x10s	700	4	2	Large cracks (hairlines) more bubbles.				
423	2x10s	700	4	2	Same + yellow stain.	T+C stronger			
424	2x10s	700	4	2	No cracks + yellow stain.	Weak T+C			
425	2x10s	700	4	2	No cracks in coating.				
426	2x10s	700	4	2	Cracks - hairlines.				
427	2x10s	700	4	2	Yellowish, dendritic structure	Stronger T+C			
428	3x10s	700	4	2	Spray blocked. Repeated	T+C			
429	3x10s	700	4	2	Purple, cracks.	T+C			

ORF

T - Tetragonal C - cubic

TABLE D9
SnCl₄·5H₂O/Alcan C71 Alumina

Plate #	Spray Cycle	Solvent	Concentration	pH	Mix Ratio	Furnace Temp (°C)	Heating Duration (min)	Results/Remarks			
								X-Ray	S.E.M	Hardness	Abrasion
75		H ₂ O/HCl	80 wt% 20 wt%	<0	3/1	850	2				
76		"	"	"	"	850	2				

D27

* Sprayed once for 5 sec.

ORF

TABLE D10
Multilayer Al(NO₃)₃·9H₂O/SnCl₄·5H₂O

Plate #	Spray Cycle	Solvent	Concentration	pH	Mix Ratio	Furnace Temp (°C)	Heating Duration (min)	Results/Remarks			
								X-Ray	S.E.M	Hardness	Abrasion
136		H ₂ O/ C ₂ H ₅ OH	(1) 20wt% (2) 80wt%	(1) 1.4 (2) .2	50/50	400	8				
137		"	"	"	"	400	8				
138		"	"	"	"	400	(1) 8 (2) 10				

D28

* Sprayed once for 5 sec.

ORF

TABLE D15 (continued)

Plate #	Spray Cycle	Furnace Temp.	Heating Duration (min)		Comments	Results			
			Initial	Between Coats		X-Ray	S.E.M.	Hardness	Abrasion
430	3x10s	700	4	2	Yellow, cracks	T+C			
434	3x10s	700	4	2	Yellow, cracks.	T+C			
431	3x10s	700	4	2	Yellow, few cracks.				
432	3x10s	700	4	2	Yellow, single direction cracks.	T+C			
433	3x10s	700	4	2	Few cracks, crystal inclusion.				

D41

T = Tetragonal C = cubic.

ORF

TABLE D16

Butyltitanate

Plate #	Spray Cycle	Solvent	Concentration	pH	Mix Ratio	Furnace Temp (°C)	Heating Duration (min)	Results/Remarks			
								X-Ray	S.E.M	Hardness	Abrasion
317	1x5s				70/30	500	6				
318	3x5s					500	6-3				
319	1x20s					500	6				
320	1x5s					400	8				

D42

ORF

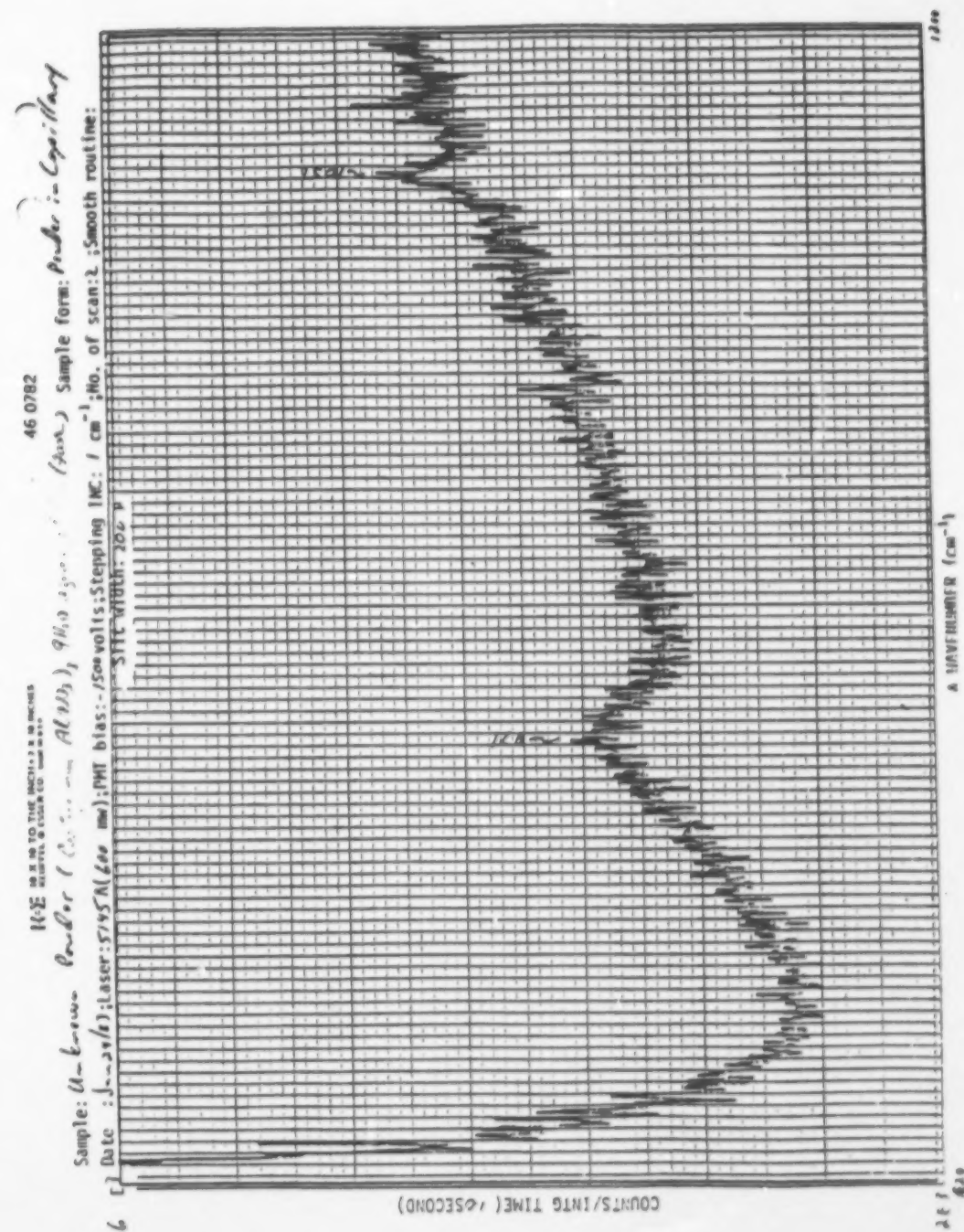
TABLE D11
n-Butylzirconate Solution (initial trial)

Plate #	Spray Cycle	Solvent	Concentration	pH	Mix Ratio	Furnace Temp (°C)	Heating Duration (min)	Results/Remarks			
								X-Ray	S.E.M	Hardness	Abrasion
267	1x5s	Butanol	16.7w%			300	10				Adhesion fair White powder
268	2x5s	"	"			300	10				Good adhesion Yellow powder
269	1x5s	"	"			200	12				Fair adhesion White powder
270	1x5s	"	"			200	12				Fair to poor adhesion White powder.
271	1x5s	"	"			250	11				Fair to poor adhesion White powder
272	1x5s	"	"			250	11				Fair adhesion Yellow/white haze w. very little powder.
273	1x5s	"	"			300	10				Fair to good adhesion White haze.
274	1x5s	"	"			300	10				Fair to good adhesion White haze.
275	1x5s	"	"			350	9				No coating.

* Sprayed once for 5 sec.

ORF

APPENDIX E Raman Spectra



ORF

TABLE D11 (continued)

Plate #	Spray Cycle	Solvent	Concentration	pH	Mix Ratio	Furnace Temp (°C)	Heating Duration (min)	Results/Remarks			
								X-Ray	S.E.M	Hardness	Abrasion
276		Butanol	16.7w%			350	9				Fair adhesion White powder.
277		"	"			350	9				No coating.
278	1x5s	"	28.6			350	9				Fair to good adhesion. V. light haze.
279	1x5s		100%			350	9				Fair adhesion V. heavy white in centre. Yellow edges.
280	1x3s		100%			400	8				Good chemical bond. Hazy in centre. Coloured rings outside.
281			100%			300	10				Poor adhesion White powder build up in centre.
282	1x5s	Butanol	50 w%		50/50	300	10				Poor adhesion White powder build up in centre.
283	1x5s	"	60/40		60/40	300	10				N/R

* Sprayed once for 5 sec.

ORF

TABLE D11 (continued)

Plate #	Spray Cycle	Solvent	Concentration	pH	Mix Ratio	Furnace Temp (°C)	Heating Duration (min)	Results/Remarks				
								X-Ray	S.E.M	Hardness	Abrasion	Appearance
284	1x5s		100%			400	8				No coat.	
285	1x10s					400	8				Fair adhesion Brown yellow grain like structure.	
286	1x5s		100%			450	7		574-608.4	inside 574 outside 608	Haze in centre 2 sets colored ring on outside.	
287	3x5s		100%			450	7		336.4-604.9	inside 336.4 outside 604.9	Good adhesion Hazy in centre Colored rings outside.	
288	1x5s 1x7s		100%			500	6		280-594.4	inside 280- outside 594.4	Hazy, some rings in centre some rings outside.	
289	1x10s					600	4		161		Transparent purple adhesion, good Yellow outside very light.	
290	1x10s					650	6				Adhesion good Transparent, purple centre Yellow outside No rings.	

* Sprayed once for 5 sec.

TABLE D11 (continued)

D32

Plate #	Spray Cycle	Solvent	Concentration	pH	Mix Ratio	Furnace Temp (°C)	Heating Duration (min)	Results/Remarks				
								X-Ray	S.E.M	Hardness	Abrasion	Appearance
291						750	6					Deformed.
292	1x10s		100%			750	2					
293	2x5s		100%			650	4					Purple at centre. Good adhesion.
294	2x10s		100%			650	6					Good adhesion purple centre wide rings.
295	3x10s		100%			650	6					"
296	2x5s		100%			650	6					"
297	1x10s		100%			800	1					Adhesion fair Brown at centre white rings at edges. Runs
298	1x5s		100%			800	1					Purple centre Yellow outside
307	1x10s		100%			500	6					White powder. poor adhesion
308	1x10s		100%			400	8					"
309	1x10s		100%			550	6					"
310	10x2s		100%			350	7					White powder fair adhesion

* Sprayed once for 5 sec.

TABLE D11 (continued)

Plate #	Spray Cycle	Solvent	Concent-ration	pH	Mix Ratio	Furnace Temp (°C)	Heating Duration (min)	Results/Remarks			
								X-Ray	S.E.M	Hardness	Abrasion
311	5x5s		100%			450	7				White powder fair adhesion
312	5x2s		100%			800	3				White powder poor adhesion
313			100%			800	3.5				White powder fair adhesion
314			100%			800	3				White powder poor adhesion
321	1x10s 20s hold 1x1sec		100%			500	6				
322	1x10s		100%			550	6				
323	1x10s		100%			550	6				
324			100%			600					
325	1x10s 4x (1x5s 5s hold 1x5s)		100%			600	6-3				Pressure 80psi
326	1x10s 10s off 1x10s		100%			300	10				Pressure 80psi

* Sprayed once for 5 sec.

ORF

TABLE D11 (continued)

Plate #	Spray Cycle	Solvent	Concent-ration	pH	Mix Ratio	Furnace Temp (°C)	Heating Duration (min)	Results/Remarks				
								X-Ray	S.E.M	Hardness	Abrasion	Appearance
327	1x10s hold 1x10s		100%			400	8					Pressure 80psi
328	1x5s 2s hold 1x5s		100%			450	7					Pressure 80psi
329			100%			450	7					Pressure 70psi
330	1x10s RH 1x5s		100%			500	6					Pressure 70psi good coat cracked
331	1x10s RH 1x10s		100%			450	12					

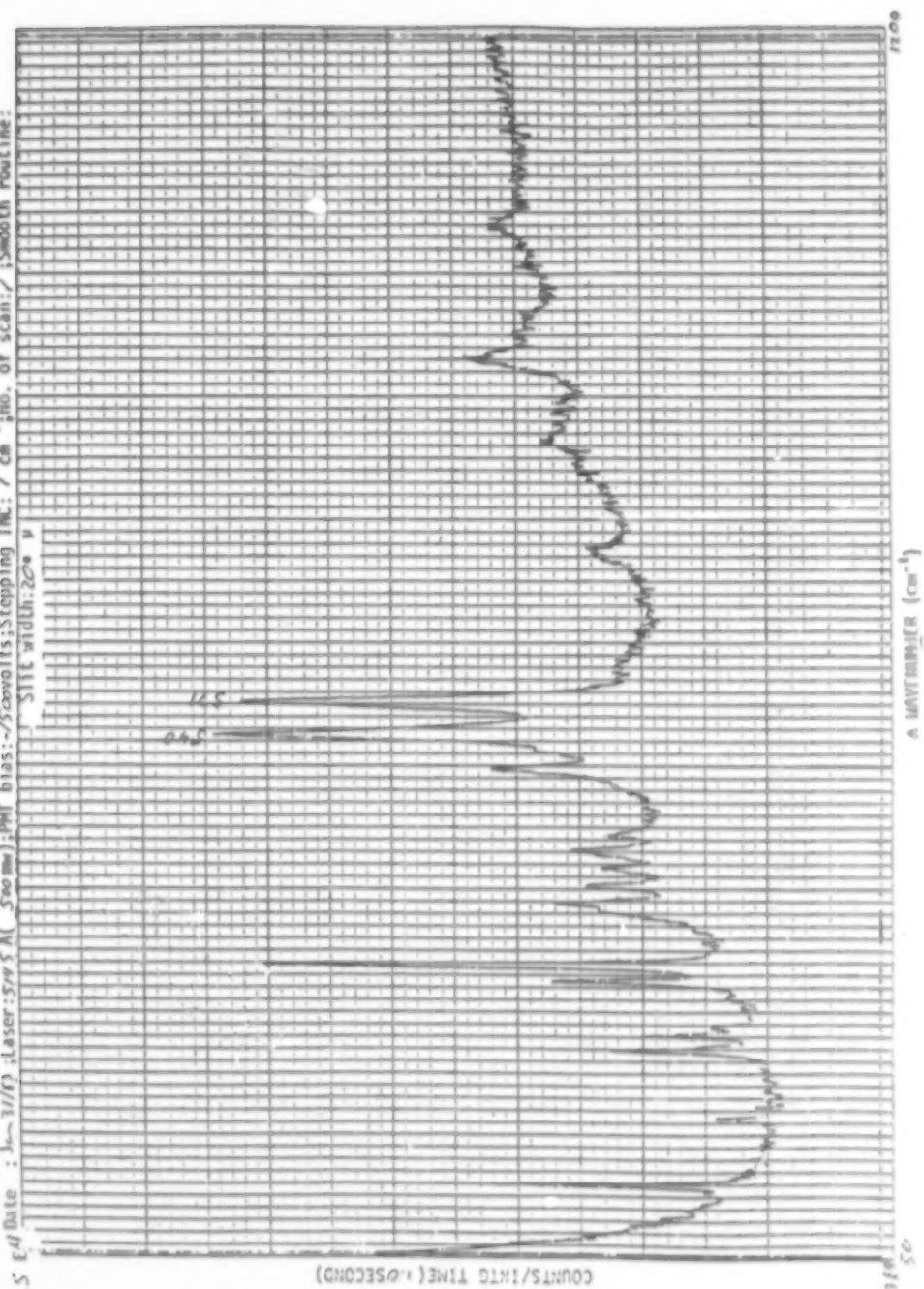
* Sprayed once for 5 sec.

ORF

46 0782

NOTE: 10.00 TO THE INCHES 2.5 TO INCHES

Sample: *all on h*
 Date: *10-11-91* Laser: *500 mW* PHE bias: *500 mV* Stopping INC: *2 cm⁻¹* No. of scan: *1* Smooth routine: *1*
 Slit width: *200 μ*



ORF

APPENDIX F

Differential Scanning Calorimetry
 (from Report 67059-6)

ORF

PART NO. 990527

RUN NO. _____ DATE 3/10/83
 OPERATOR SL
 SAMPLE Aluminum Oxide
 ATM N₂
 FLOW RATE 100 cc/min

T-AXIS

PROG. RATE, °C/min 10
 RANGE, °C/cm 25
 HEAT ☒ COOL ☐ ISO ☐
 SHIFT, cm +10
 TIME, min/cm 25

DSC

200 μ W/mV

DTA

50 mK/mV

RANGE, mV/cm 10

WEIGHT, mg 11.3

REFERENCE empty Au pan

TGA 50 μ g/mV DTG 50 μ g/(min mV)

SUPPRESSION, mg

RANGE, mV/cm

WEIGHT, mg

TIME CONST., sec

dV

TMA 1 μ m/mV DTM 0.1 μ m/(min mV)

MODE

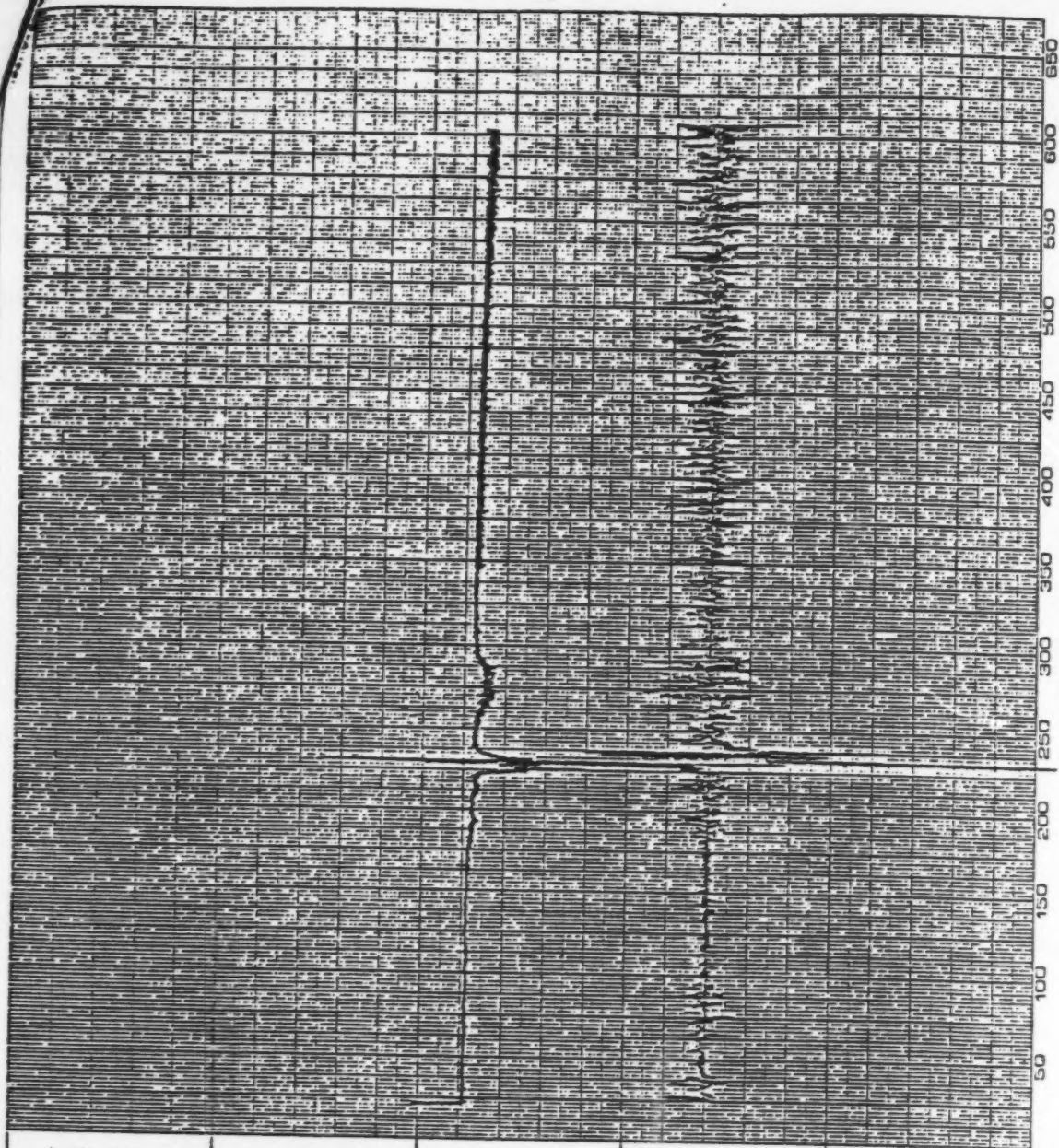
RANGE, mV/cm

SAMPLE SIZE

LOAD, g

dV

F1



TEMPERATURE, °C (CHROMEL/ALUMEL)

TECHNICAL SERVICES

TECHNICAL SERVICES

TECHNICAL SERVICES

APPENDIX G

Abrasion Tests

APPENDIX B

ASTM Standard C158-80



Standard Methods of FLEXURE TESTING OF GLASS (DETERMINATION OF MODULUS OF RUPTURE)¹

This Standard is issued under the fixed designation C 158; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval.

1. Scope

1.1 These methods cover the determination of the modulus of rupture in bending of glass and glass-ceramics.

1.2 These methods are applicable to annealed and prestressed glasses and glass-ceramics available in varied forms. Alternative test methods are described; the method used shall be determined by the purpose of the test and geometric characteristics of specimens representative of the material.

1.2.1 Method A is a test for modulus of rupture of flat glass.

1.2.2 Method B is a comparative test for modulus of rupture of glass and glass-ceramics.

1.3 The methods appear in the following order:

	Sections
Method A	6 to 9
Method B	10 to 14

2. Applicable Documents

2.1 ASTM Standards:

C 148 Polariscopic Examination of Glass Containers²

E 4 Load Verification of Testing Machines

E 380 Metric Practice³

3. Significance

3.1 For the purpose of this test, glasses and glass-ceramics are considered brittle (perfectly elastic) and to have the property that fracture normally occurs at the surface of the test specimen from the principal tensile stress. The modulus of rupture is considered a valid meas-

ure of the tensile strength subject to the considerations discussed below.

3.2 It is recognized that the modulus of rupture for a group of test specimens is influenced by variables associated with the test procedure. These include the rate of stressing, test environment, and the area of the specimen subjected to stress. Such factors are specified in the test procedure or required to be stated in the report.

3.3 It is also recognized that the variables having the greatest effect on the modulus of rupture value for a group of test specimens are the condition of the surfaces and glass quality near the surfaces in regard to the number and severity of stress-concentrating discontinuities or flaws, and the degree of prestress existing in the specimens. Each of these can represent an inherent part of the strength characteristic being determined or can be a random interfering factor in the measurement.

3.4 Method A is designed to include the condition of the surface of the specimen as a factor in the measured strength. It is, therefore, desirable to subject a fixed and significant area of the surface to the maximum tensile stress. Since the number and severity of surface flaws in glass are primarily determined by manufacturing and handling processes, this method is limited to products from which

¹ These methods are under the jurisdiction of ASTM Committee C-14 on Glass and Glass Products.

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² Annual Book of ASTM Standards, Part 17.

³ Annual Book of ASTM Standards, Parts 10, 14, 32, 35, and 41.

⁴ Annual Book of ASTM Standards, Part 41.



specimens of suitable size can be obtained with minimal dependence of measured strength upon specimen preparation techniques. This method is thus designated as a Test for Modulus of Rupture of Flat Glass.

3.5 Method B describes a general procedure for test, applicable to specimens of rectangular or elliptical cross section. This method is based on the assumption that a comparative measurement of strength on groups of specimens is of significance for many purposes, such as determining the effect of environment or stress duration, or the effectiveness of varied prestressing techniques or strengths characteristic of glass-ceramics of differing composition or heat treatment. In this method the surfaces of the specimens are not assumed to be characteristic of a product or material, but are considered to be determined by the procedures used to prepare the specimens. Though the stated procedure permits a wide variation in both specimen size and test geometry, it is necessary to use identical test conditions and equivalent procedures for specimen preparation to obtain comparable strength values. The use of a controlled abrasion of the specimen as a final normalizing procedure is recommended for such comparative tests.

3.6 A comparative abraded strength, determined as suggested in Method B, is not to be considered as a minimum value characteristic of the material tested nor as directly related to a maximum attainable strength value through test of specimens with identical flaws. The operationally defined abrasion procedure undoubtedly produces flaws of differing severity when applied to varied materials, and the measured comparative strengths describe the relative ability to withstand externally induced stress as affected by the specific abrasion procedure.

4. Definitions and Descriptions of Terms

4.1 *abraded*—All test specimens designated as abraded shall have had at least a portion of the area of maximum surface tensile stress subjected to an operationally defined procedure for mechanical abrasion. The severity and uniformity of abrasion should be sufficient to ensure origin of failure substantially in the region of maximum stress.

4.2 *annealed glass*—Specimens representative of the annealed state shall not have a temper or degree of residual stress resulting from prior thermal treatment in excess of the following limits when measured polarimetrically (see Annex A1):

4.2.1 Specimens of rectangular section shall not have a tensile stress at the midplane of more than 200-psi (1.38-MPa) nor more than 400-psi (2.76-MPa) compression at the surface.

4.2.2 Specimens in rod form may be examined by viewing through a diameter at least four diameters from an end. The *apparent* central axial tension shall not exceed 133 psi (0.92 MPa). Surface compression, if measured on sections cut from the rods, shall not exceed 400 psi (2.76 MPa) when viewed axially.

4.3 *glass-ceramics*—solid materials, predominantly crystalline in nature, formed by the controlled crystallization of glasses.

4.4 *modulus of rupture in bending*—the value of maximum tensile or compressive stress (whichever causes failure) in the extreme fiber of a beam loaded to failure in bending computed from the flexure formula:

$$S_b = M c / I$$

where:

M = maximum bending moment, computed from the maximum load and the original moment arm,

c = initial distance from the neutral axis to the extreme fiber where failure occurs, and

I = initial moment of inertia of the cross-section about the neutral axis

4.5 *Prestressed*—material in which a significant and controlled degree of compressive stress has been deliberately produced in the surfaces.

4.6 *standard laboratory atmosphere*—an atmosphere having a temperature of 23 ± 2 C and a relative humidity of $40 \pm 10\%$.

5. Apparatus

5.1 *Testing Machine*—The loading mechanism shall be sufficiently adjustable to give the required uniform rate of increase of stress. The load-measuring system shall be essentially free of inertial lag at the loading rates used and



shall be equipped with means for retaining indication of the maximum load applied to the specimen. The accuracy of the testing machine shall conform to the requirements of Methods E 4.

5.2 Bearing Edges—Cylindrical bearing edges of approximately $\frac{1}{4}$ -in. (3-mm) radius shall be used for the support of the test specimen and the application of the load. The bearing edges shall be of steel and sufficiently hardened to prevent excessive deformation under load. Two-point loading tests shall be performed with the loading member pivoted about a central transverse axis to ensure equal distribution of load between the two bearing edges. For the testing of specimens of rectangular section, both loading bearing edges and one support bearing edge also shall be pivoted laterally to compensate for irregularities of the test specimen. Figure 1 shows a suitable arrangement using pinned bearing edges. In test of specimens of a circular or elliptical section, the fixed cylindrical support edges may have a curvature of approximately 3 in. (76 mm) in the plane of the bearing edge to stabilize the alignment of the specimens. Such support edges are shown in Fig. 2.

METHOD A—TEST FOR MODULUS OF RUPTURE OF FLAT GLASS

6. Test Specimens

6.1 Preparation of Specimens—Test specimens shall be cut from the sheet stock with a diamond or a cutting wheel. Both longitudinal cuts shall be on the same original surface and none of the original edge of the sheet shall be used as a longitudinal side of the specimen. End cuts may be on either surface. The direction of cutting of half of the total number of specimens shall be perpendicular to the direction of cutting of the remainder. Specimens that must be cut from sheet stock prior to the use of a prestressing treatment shall have the corners of the longitudinal edges rounded to minimize damage to the edges in the prestressing process. All operations shall be performed with the direction of grind or polish parallel to the longitudinal axis. The radius of the corner shall not exceed $\frac{1}{16}$ in. (1.6 mm).

6.2 Size of Specimens—The specimens shall be approximately 10 in. (250 mm) in length

and $1\frac{1}{2} \pm \frac{1}{4}$ in. (38.1 ± 3.2 mm) in width. The variation in width or thickness shall not exceed 5% from one end to the other.

6.3 Number of Specimens—At least 30 specimens shall be used for one test and shall preferably be taken from several sheets, or regions of a single sheet.

6.4 Examination of Specimens—Any specimen may be rejected prior to test for observable defects considered likely to affect the modulus of rupture. To be considered representative of annealed glass the specimens must meet the requirement of 4.2.1. At least 30% of the specimens shall be examined for residual stress. If any of these fail to meet the requirement, the remainder of the specimens shall be examined and those exceeding the stated limit shall be rejected.

7. Procedure

7.1 Space the supporting edges of the test fixture 8.00 in. (200 mm) apart and centrally position the loading edges with a separation of 4.00 in. (100 mm). Break specimens having cut edges with the cutter marks on the face under compression. Carefully place each specimen in the test fixture to minimize possible damage and to ensure alignment of specimen in the fixture. The permissible maximum fiber stress due to initial load on the specimen shall not exceed 25% of the mean modulus of rupture. Load the specimen at a constant rate to failure. For annealed glass the rate of loading shall correspond to a rate of increase of maximum stress of $10\,000 \pm 2000$ psi/min (1.1 ± 0.2 MPa/s). Test prestressed glasses with the increase of maximum stress per minute between 80 and 120% of the modulus of rupture. The first six specimens of the group may be tested at a loading rate based on an estimate of the modulus of rupture and the average value for these specimens used to correct this estimate. If range of width and thickness variation in the specimens is less than 5%, the mean values may be used to represent all specimens for the purpose of calculation of rate of loading.

7.2 Determine the thickness and width of each specimen to $\pm 1\%$. To avoid damage from gaging in the critical area, take measurements prior to testing near each end with a



separation equal to the support span, and average the values. Measurements following test shall be in the uniformly stressed region of the specimen.

7.3 Determine the location of point of failure and note it as edge or face origin. Plastic or other tape of low elastic modulus⁴ may be used on the compressive surface to contain the fragmentation and allow observation of point of failure for highly prestressed specimens. Report all values, although segregation of edge break values is permitted.

8. Calculation

8.1 Calculate the modulus of rupture, initial maximum fiber stress, and rate of increase of stress as follows:

8.1.1 Modulus of rupture:

$$S = 3 L_0 a / b d^2$$

8.1.2 Maximum stress due to initial load if present:

$$S_0 = 3 L_0 a / b d^2$$

8.1.3 Rate of increase of maximum stress:

$$R = (3a/bd^2) \cdot (\Delta L / \Delta t)$$

$$R = (S - S_0) / t$$

where:

S = modulus of rupture,

S_0 = maximum fiber stress due to initial load if present,

R = rate of increase of maximum fiber stress,

L = breaking load including initial load,

L_0 = initial load,

a = moment arm or distance between adjacent support and loading edges,

b = width of specimen,

d = thickness of specimen,

t = time from start of continuous loading to rupture, min, and

$\Delta L / \Delta t$ = rate of increase of load.

9. Report

9.1 The report shall include the following:

9.1.1 Method of test used,

9.1.2 Identification of the glass tested, including any special treatment (For specimens derived from manufacturing processes that are asymmetric in nature (for example, the float process), the side of the sheet placed in tension during test shall be identified, if possible),

9.1.3 Classification as annealed or prestressed glass,

9.1.4 Test environment if other than standard laboratory atmosphere,

9.1.5 Rate of increase of maximum stress,

9.1.6 Value of the modulus of rupture for each specimen and designation of point of failure as edge or face, and

9.1.7 Average value of the modulus of rupture for the group and the standard deviation estimate of the mean. Separate values may be determined for edge and face origins.

NOTE 1—See Annex A3 for conversion from inch-pound units and other non-SI units to SI units.

METHOD B—COMPARATIVE TEST FOR MODULUS OF RUPTURE OF GLASS AND GLASS-CERAMICS

10. Test Specimens

10.1 Preparation of Specimens:

10.1.1 Specimens of rectangular cross section may be prepared by any sequence of conventional operations such as cutting, sawing, grinding, or polishing. Longitudinal edges on the face to be placed in tension should be chamfered or rounded. The corner radius shall be a minimum value sufficient to eliminate edge breaks and shall not exceed one tenth the thickness in specimens approaching a square cross section. Specimens shall have equivalent size and manufacturing procedures in groups to be compared. The specimen length shall be at least 1/2 in. (12.7 mm) greater in length than the support span used in test. The width to thickness ratio is recommended to be between 2:1 and 10:1. The minimum width shall be 1/8 in. (9.5 mm), although specimens of greater width are desirable. The variation in width or thickness shall not exceed 3% over the length of the specimen equal to the support span.

10.1.2 Specimens in rod form may be prepared as drawn cane or by procedures such as core drilling and centerless grinding. Equivalent sizes and manufacturing procedures shall be used on specimens for comparison. The specimen length shall be at least 1/2 in. (12.7 mm) greater than the support span used in the test. The diameter shall be optional, with a minimum value of 1/8 in. (4.76 mm). The variation in a measured diameter shall not exceed 3% over the length of the specimen equal to the support span. The length-to-diameter ratio shall be greater than 10:1. Specimens

⁴Scotch Brand plastic tape, Catalog No. 191-A, has been found suitable for this purpose.

mens may be elliptical in section, but the minor diameter shall not be less than 80% of the major diameter. The specimen shall be straight within $\frac{1}{8}$ in. in 4 in. (or 3 mm in 100 mm). The curvature shall be limited to a single plane containing the major or minor diameter of any ellipticity, if this ellipticity exceeds 5%.

10.2 Number of Specimens:

10.2.1 It is recommended that at least 30 specimens shall be available for one test if a controlled abrasion procedure is not used as a normalizing procedure. Utilization of fewer specimens is permissible if conclusions of satisfactory statistical validity are possible, though a minimum of ten specimens is required.

10.2.2 At least 10 specimens shall be used for one test if a controlled abrasion is used to normalize the surface condition of the specimens.

10.3 Examination of Specimens:

10.3.1 Any specimens may be rejected prior to testing for defects considered likely to affect the modulus of rupture.

10.3.2 Specimens of glass described as annealed must meet the requirements of 4.2. At least 30% of the specimens shall be examined for residual stress. If any of these are not within the requirements, the remainder of the specimens shall be examined and those exceeding the stated limit shall be rejected.

11. Test Conditions

11.1 *Specimens of Rectangular Section*—The moment arm or separation of adjacent support and loading edges shall be greater than the width of the specimen and at least four times the thickness of the specimen. The separation of the loading edges shall be not less than $\frac{1}{4}$ in. (19 mm) and at least three times the thickness of the specimen. Within these limitations the test geometry may be adjusted to accommodate the loading range of the testing machine. It should be noted that for highly prestressed materials the possibility of excessive flexure (greater than approximately one half the specimen thickness) and end slope may exist at large span-to-thickness ratios.

11.2 *Specimens of Round or Elliptical Section*—The moment arm or separation of support and loading edges shall be at least four times the vertical diameter of the specimen. The separation of the loading edges shall be not less than $\frac{1}{4}$ in. (19 mm) and at least three

times the vertical diameter. Within these limitations the test geometry may be adjusted to accommodate the loading range of the testing machine. It should be noted that low moment arm-to-diameter ratios may result in undesirable high contact stresses from the bearing edges.

11.3 *Single Point Loading*—Although not generally recommended, single-point loading is acceptable under the following circumstances:

11.3.1 For establishing experimental correlation with existing single-point loading data, and

11.3.2 When the distribution of glass defects or flaws (see 3.3) is such that their presence is unavoidable within the minimum distance between the loading points as specified in 11.1 and 11.2. Such defects or flaws must be non-characteristic to the glass composition and of no primary interest to the strength study.

11.3.3 For single-point loading, make the separation of the loading edges zero while maintaining all other requirements in 11.1 and 11.2.

12. Procedure

12.1 Measurement of Specimens:

12.1.1 Individually measure specimens of rectangular section for width and thickness to 0.001 in. (0.02 mm). If a controlled abrasion is not utilized, limit measurements prior to the test to regions near the ends, separated by a distance equal to the support span, and record the average value.

12.1.2 Place specimens of elliptical or round section on a set of support edges of appropriate span, and note a normal equilibrium position. Mark the vertical axis, and measure the vertical and horizontal diameters to 0.001 in. (0.02 mm). If a controlled abrasion is not utilized, limit the measurements prior to testing to regions near the ends at a separation equal to the support span, and record the average values.

12.2 *Loading to Failure*—Carefully locate the specimens in the test fixture to minimize damage to the specimen and to ensure alignment with axis of the fixture. Specimens in rod form shall have the indicated vertical axis so located during test. For specimens of rectangular section, place the abraded face in tension. Do not allow the initial load on the specimen to produce a maximum fiber stress in excess of 25% of the mean modulus of rupture. Uni-



formly apply the load until failure occurs. For annealed glass, the rate of loading shall correspond to a rate of increase of maximum stress of $10\,000 \pm 2000$ psi/min (1.1 ± 0.2 MPa/s). For prestressed glasses and glass-ceramics, the increase of maximum stress per minute shall be between 80 and 120% of the modulus of rupture. The first 20% of the group may be tested at a loading rate based on an estimate of the modulus of rupture and the average value for these specimens used to correct this estimate. For specimens of rectangular section, determine and record the point of failure as edge or face origin for specimens without abrasion, and record it as to occurrence in abraded area for specimens having such abrasion. The use of plastic or other low-modulus tape^a is permitted on the compressive surface to contain the fragmentation and permit observation of point of failure. Report all values, although segregation into appropriate classification is permitted.

13. Calculation

13.1 Calculate the modulus of rupture, initial maximum fiber stress, and rate of increase of stress as follows:

13.1.1 Modulus of rupture for specimens of rectangular section:

$$S = 3La/bd^2$$

For specimens of elliptical section:

$$S = 5.09 La/bd^2$$

13.1.2 Stress due to initial load if present for specimens of rectangular section:

$$S_0 = 3L_0a/bd^2$$

For specimens of elliptical section:

$$S_0 = 5.90 L_0a/bd^2$$

13.1.3 Rate of increase of maximum stress for specimens of rectangular section:

$$R = (3a/bd^2) \cdot (\Delta L/\Delta t)$$

For specimens of elliptical section:

$$R = (5.09/bd^2) \cdot (\Delta L/\Delta t)$$

For specimens of any section:

$$R = (S - S_0)/t$$

where:

S = modulus of rupture,

S_0 = maximum fiber stress due to initial load, if present,

R = rate of increase of maximum fiber

stress,

L = breaking load,

L_0 = initial load,

a = moment arm or separation of adjacent loading and support edges,

b = width of specimen or horizontal diameter,

d = thickness of specimen or vertical diameter,

t = time from start of continuous loading to rupture, min, and

$\Delta L/\Delta t$ = rate of loading.

14. Report

14.1 The report shall include the following:

14.1.1 Method of test used,

14.1.2 Identification of the material tested, including any special treatment,

14.1.3 Classification as annealed or prestressed material,

14.1.4 Form and size of specimens,

14.1.5 Method of preparation of specimens and abrasion procedure used, if any,

14.1.6 Test environment if other than standard laboratory atmosphere,

14.1.7 Test geometry and conditions of loading (single-point or two-point).

14.1.8 Rate of increase of maximum stress.

14.1.9 Value of the modulus of rupture for each specimen (the point of failure for specimens of rectangular section shall be indicated with regard to face or edge origin for specimens not subjected to abrasion, and with regard to occurrence in the abraded area for specimens subjected to a controlled abrasion), and

14.1.10 Average value of the modulus of rupture for the group and the standard deviation estimate for the mean. Separate values may be determined for the specimens segregated by point of origin (Note).

15. Precautions

15.1 Care should be exercised in all handling of specimens to avoid the introduction of random and severe flaws.

15.2 Abrasion of specimens of rectangular section should be performed so that corners are not subjected to abrasion. Abrasion should be limited to the region of uniform tensile stress between the loading edges, and it should cover a significant fraction of this area.

15.3 Following an abrasion procedure, a



minimum time of 1 h must elapse before taping or testing of specimens (See Annex A2.2).

15.4 Deflectometers, if used during testing, should not contact the tension face of the specimen.

15.5 If tests are performed at temperatures

deviating from ambient, it is necessary to allow the specimen to reach thermal equilibrium to eliminate the presence of thermally induced stresses in the specimen. The report should indicate the thermal history prior to testing.

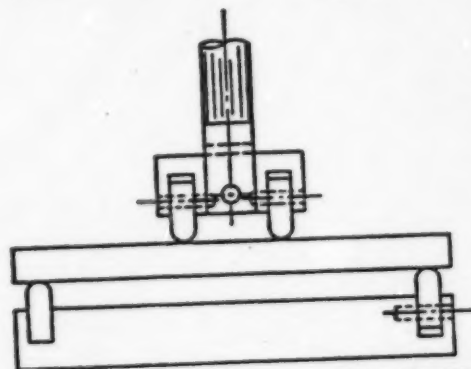


FIG. 1 Pinned Bearing Edges.

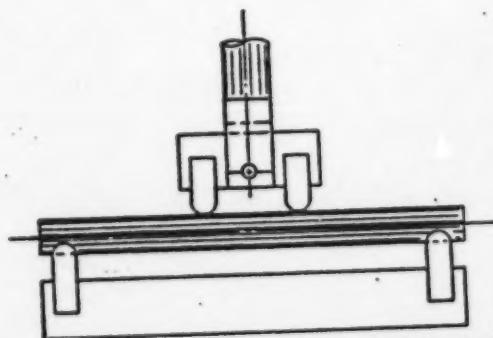
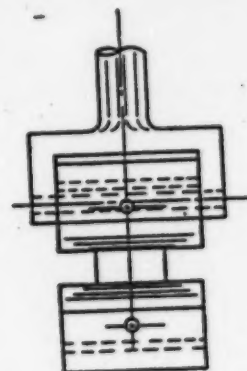
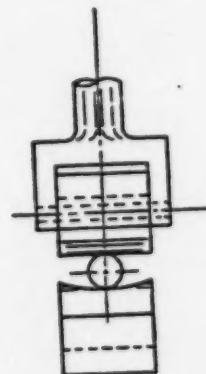


FIG. 2 Fixed Cylindrical Support Edges.



ANNEXES

A1. DETERMINATION OF RESIDUAL STRESS

A1.1 The required determination of residual stress can be carried out with either a polarizing microscope or a polariscope (polarimeter) equipped with suitable means for quantitative measurement of birefringence. Suitable devices include the Berek or Babinet compensators as well as the combination of a quarter-wave plate and rotating analyzer referred to as the Sénarmont (1)* or Friedel (2) compensator. Method B of Method C 148 requires the use of the

latter form and includes a description of a typical apparatus.

A1.2 With all methods of compensation, the measurements are made with the polarizer and analyzer crossed to produce a dark field. The path of

*The boldface numbers in parentheses refer to a list of references located at the end of these Annexes.



the light through the specimen shall be perpendicular to the longitudinal axis of the specimen, and for a specimen of rectangular shape shall be parallel to the faces of the specimen that will be placed in tension and compression. The orientation of the specimen must be with the longitudinal axis of the specimen at 45 deg, with the plane of polarization of the polarizer. If not known, the plane of polarization can be determined as being parallel to the longitudinal axis of the specimen when this axis is rotated between the crossed polarizer and analyzer to produce minimum brightness in the specimen. After proper orientation of the specimen, the magnitude of the birefringence, or relative retardation in nanometers, is determined for the light passing through the appropriate region of the specimen. The longitudinal stress may then be determined as follows:

$$S = R/kt$$

where:

S = longitudinal stress, psi (or Pa),

k = stress optical coefficient, nm/in.·psi (or nm/m·Pa),

R = relative retardation, nm, and

t = light path length in specimen, in. (or m).

A1.3 The stress-optical coefficient shall be determined for the glass being measured. For common soda-lime glasses the value is approximately 0.45 nm/in. for stress of 1 psi (2.57×10^{-3} nm/m·Pa). The relative retardation is proportional to the algebraic difference of the principal stresses in the plane normal to the light path, averaged over this light path. The method of calculation assumes the principal stress normal to the faces of the specimen to be zero. This assumption is valid for specimens used in Method A, or otherwise prepared such that major temperature gradients during cooling have been perpendicular to the faces of the specimen. This may not be true for all specimens prepared for Method B, and observations of birefringence should be performed with the light path perpendicular to both test surface and edge of the specimen. Round specimens being examined should be rotated about the longitudinal axis to obtain maximum retardation reading.

A1.4 Crystal compensators shall be calibrated through the use of monochromatic light (commonly the 546 nm Hg radiation) and then may be used with white-light sources to ensure proper determination of integral order of retardation. The rotating analyzer is self-calibrated if used with monochromatic light (180-deg rotation = 1 wavelength of retardation), but it presents difficulties if used with white-light sources. The retardation per degree rotation is affected by the spectral distribution of the source and the sensitivity of the eye as well as the color used by the observer to determine extinction. It is recommended that the appropriate constant be determined, for the specific instrument and observation technique, by use of a loaded beam or specimen of known relative retardation. This technique will also permit determination of the sign of the observed stress (tension or compression) for a specified orientation of the specimen.

A1.5 Precautions:

A1.5.1 In using compensation techniques limited to one wavelength of relative retardation such as the Friedel method, it is necessary to determine that the relative retardation is actually less than one wavelength. The existence of more than one wavelength of retardation will be indicated by the presence of fringes higher than zero order. These fringes will be colored when observed with white light, though black with monochromatic light. The existence of retardations of this order of magnitude would occur in the standard specimen for Method A at a residual stress level of approximately 850 psi (5.86 MPa) for a soda-lime glass, and at lower stress levels for glasses having a higher stress optical-coefficient.

A1.5.2 The measurement of birefringence at surfaces of specimens may be affected by the characteristics of the instrument used. The observed image is formed by cones of rays passing through the specimen. The measured retardation is thus related to an average retardation over areas included within the cone centered on the point observed in the specimen. At an edge this may result in a lowered retardation value. The effect is increased in specimens of long light path and may be significant for microscope systems using convergent illumination and objectives of high aperture.

A2. ABRASION PROCEDURES

A2.1 *Methods of Abrasion*—Many procedures for normalizing or controlling the surface defect condition of glass specimens or articles used for strength tests have been reported in the literature (3,4). A common practice in the industry has involved the use of a specified abrasive paper or cloth. Some procedures have been designed to introduce a single controlled size defect by an indentation or impact procedure or have attempted to introduce a single oriented scratch by a mechanical device. For the purpose of Method B, any procedure producing suitable consistency of individual test values would be satisfactory. Standard deviation estimates of means should not exceed approximately 5%. Following are several examples of abrasion procedures that have resulted in satisfactory statistical measures of dispersion for test groups and that

are suitable for use when many specimens are to be abraded. A discussion of other abrasions and an alternative grit blast procedure can be found in the literature (3,4).

A2.2 *Aging of Abrasion*—Following the use of any procedure for controlled abrasion it is necessary to control the modification of severity of the abrasion that occurs when the abraded specimen is exposed to a humid atmosphere (5). For comparative strength values it is necessary that the environment and time between abrasion and test be uniform for the test groups.

A2.3 Sandblast Abrasion Procedure for Specimens of Rectangular Section:

A2.3.1 *Apparatus*—Figure A1 illustrates the general design of the apparatus.

A2.3.2 *Abrasive Material*—The abrasive used is



Berkeley sand.^{*} The fraction passing through a No. 70 (212- μ m) U.S. Standard Sieve and retained on a No. 100 (150- μ m) sieve is utilized in this abrasion procedure.

A2.3.3 Procedure:

A2.3.3.1 The air pressure is regulated to 40 psi (276 kPa) as determined by a pressure gage mounted on a standard 1/4-in. pipe tee at the end of the air inlet pipe.

A2.3.3.2 An appropriate rubber-faced mask is utilized to eliminate glass-to-metal contacts, and control the area of specimen subject to sandblast.

A2.3.3.3 The mask and specimen assembly is centered on the opening of the sandblast apparatus.

A2.3.3.4 The air is turned on, and after air flow is established, a measured 5 cm³ of sand is dumped into the center of the funnel. It is necessary to ensure that the sand feeds from the funnel and not from the container from which it is dumped.

A2.3.3.5 The air flow is continued for 5 s after the introduction of the sand as determined by the audible variation in air flow.

A2.3.3.6 The specimen is removed and the process repeated for the next specimen.

A2.3.4 Precautions:

A2.3.4.1 It is necessary to avoid scratching the specimens with sand particles. This requires removal of sand from mask surfaces before contacting the specimen.

A2.3.4.2 After a sandblast, a residue of sand is frequently observable on the specimen face. The abraded face should, therefore, not be placed in contact with surfaces as the specimen is stored before test.

A2.3.4.3 Decentering of the abrasion density may be associated with shift of the vertical air inlet tube. Centering of this tube should then be verified.

A2.4 Grit Blast Abrasion for Specimens of Rectangular Section:

A2.4.1 **Apparatus**—Figure A1 illustrates the general design of the apparatus.

A2.4.2 **Abrasive Material**—The abrasive used is silicon carbide grain. The material is obtained as No. 30 grit.

A2.4.3 Procedure:

A2.4.3.1 The air pressure is regulated to 10 psi (69 kPa) as determined by a pressure gage mounted on a standard 1/4-in. pipe tee at the end of the air inlet pipe.

A2.4.3.2 An appropriate rubber-faced mask is utilized to eliminate glass-to-metal contacts, and control the area of the specimen subject to sandblast.

A2.4.3.3 The mask and specimen assembly is centered on the opening of the sandblast apparatus.

A2.4.3.4 The air is turned on, and after air flow is established, a measured 1 cm³ of abrasive is dumped into the center of the funnel.

A2.4.3.5 The air flow is continued for 5 s after the introduction of the new abrasive.

A2.4.3.6 The specimen is removed and the process repeated for the next specimen.

A2.4.4 Precautions:

A2.4.4.1 It is necessary to avoid scratching the specimen with abrasive particles. This requires removal of abrasive particles from mask surfaces before contacting the specimen.

A2.4.4.2 After abrasion a residue of grit particles remains on the specimen. These can be shaken from the specimen.

A2.4.4.3 Decentering of the abrasion density may be associated with shift of the vertical air inlet tube. Centering of this tube should then be verified.

A2.5 Tumble Abrasion Procedure for Specimens of Elliptic Section:

A2.5.1 **Apparatus**—Roller-type ball mill to rotate No. 0 (1/2 gal) ball mill jars at 90 to 100 rpm, time switch to operate ball mill for 15-min period.

A2.5.2 **Abrading Material**—The abrading material shall be silicon carbide, 30-grit.

A2.5.3 Procedure:

A2.5.3.1 A charge of 200 cm³ of the silicon carbide is placed in the ball mill jar.

A2.5.3.2 A preconditioning of the silicon carbide is carried out by rotating the jar for 30 min after ten surplus specimens have been added to the jar.

A2.5.3.3 Abrasion of the specimens for test is performed by rotation of the jar for 15 min with the jar containing the "conditioned" silicon carbide and a group of ten specimens.

A2.5.3.4 Abrasion procedure is repeated using successive groups of ten specimens until ten groups have been abraded in the jar.

A2.5.3.5 The silicon carbide is then removed, a fresh charge of 200 cm³ is added to the jar and preconditioned in accordance with A2.5.3.2.

A2.5.4 Precautions:

A2.5.4.1 The severity of the abrasion resulting from this process is dependent on the size and weight of the specimens added to the jar. The procedure was initiated for nominal 1/4-in. diameter specimens, for which a rapid method of abrasion was desired. Relative strength of groups of specimens of the same cross-sectional area is obtained.

A2.5.4.2 The length of specimen is limited to 4 1/2 in. (114 mm) for the No. 0 jar.

^{*} Berkeley Sand is available from the Pennsylvania Glass Sand Co.

A3. CONVERSION OF UNITS

A3.1 For conversion to SI units from inch-pound units or other non-SI units the following have been derived from and rounded from the conversion factors given in Metric Practice E 380:

To Convert From	To	Multiply by
pound-force (lbf)	newton (N)	4.448

kilogram-force (kgf)	newton (N)	9.807
inch (in.)	metre (m)	2.540×10^{-2}
pound-force/inch ²	pascal (newton/metre ² , Pa)	6.895×10^3
(psi)		
kgf/millimetre ²	pascal (Pa)	9.807×10^3
(kgf/mm ²)		

REFERENCES

- (1) Rawson, H., "A Note on the Use of the Senarmont Method for Measuring Stresses in Glass" *Journal of the Society of Glass Technology*, JSGLA, Vol 42, 1958, pp. 119-124.
- (2) Durelli, A. J., and Riley, W. F., *Introduction to Photoelasticity*, Prentice-Hall, Inc., Englewood Cliffs, N. J.
- (3) Mould, R. E., and Southwick, R. D., "Strength and Static Fatigue of Abraded Glass Under Controlled Ambient Conditions: I, General Concepts and Apparatus," *Journal of the American Ceramic Society*, JACTA, Vol 42, No. 11, 1959, pp. 542-547.
- (4) Mould, R. E., and Southwick, R. D., "Strength and Static Fatigue of Abraded Glass Under Controlled Ambient Conditions: II, Effect of Various Abrasions and the Universal Fatigue Curve," *Journal of the American Ceramic Society*, JACTA, Vol 42, No. 12, 1959, pp. 582-592.
- (5) Mould, R. E., "Strength and Static Fatigue of Abraded Glass Under Controlled Ambient Conditions: III, Aging of Fresh Abrasions," *Journal of the American Ceramic Society*, JACTA, Vol 43, No. 3, 1960, pp. 160-167.

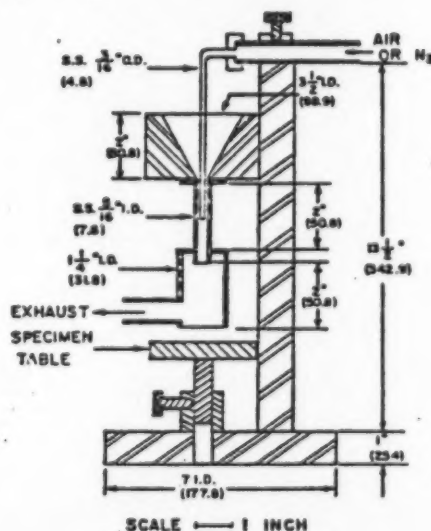


FIG. A1 Abrading Device.

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APPENDIX H
Electron Micrographs and EDX-Ray Spectra

Figure 1a

E.D. X-Ray Spectra

Job Number 83528 Date June 17/83

Client: W. Sae Company S.C.

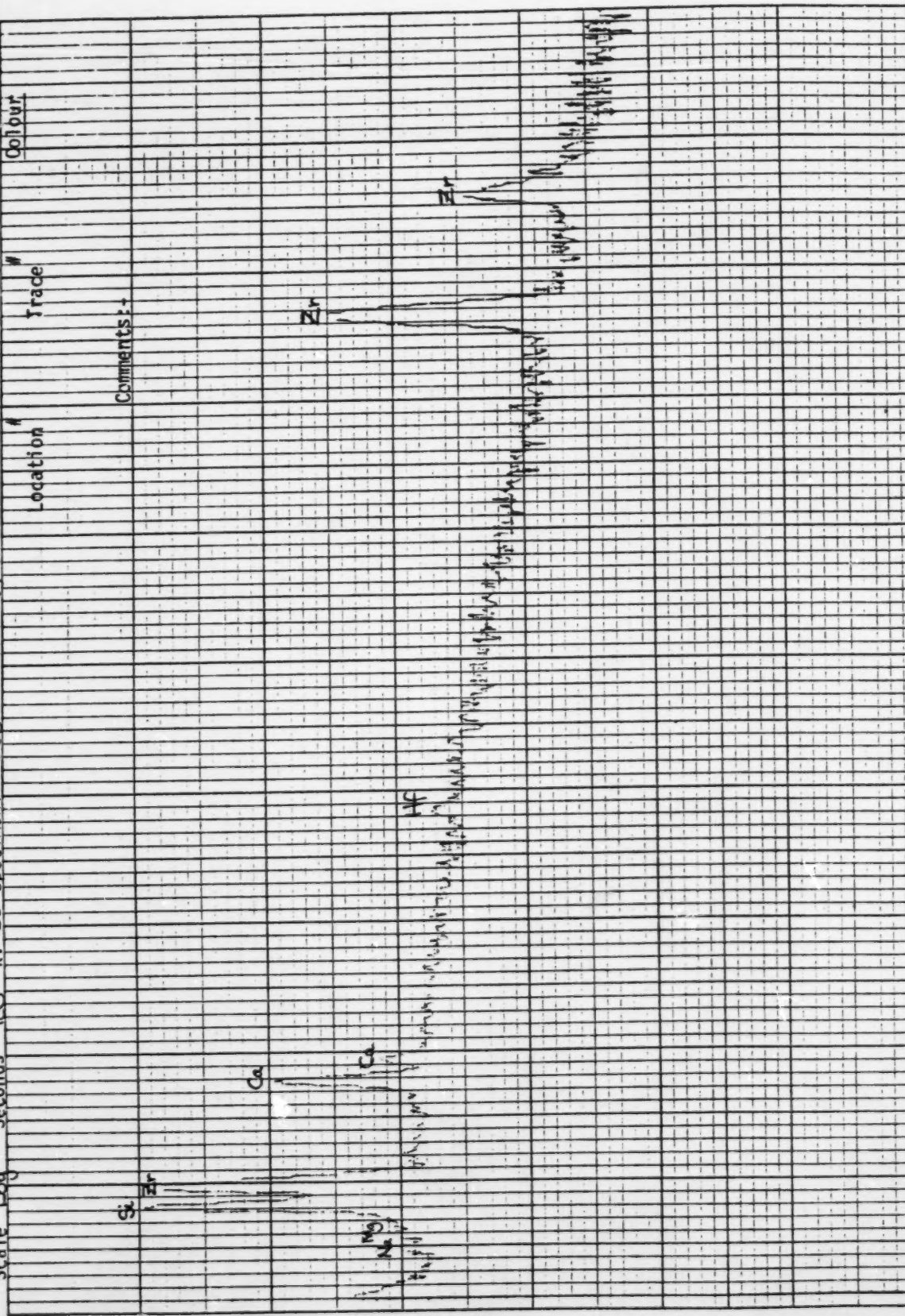
Region: Location

Trace

Scale Log

Seconds 180 kV 30 Specimen: 383

Comments:-



ORF

Figure H2(b)

H3

DATE 11, 1985

SPECTRUM 83598-432 383

ENERGY	COUNTS	X-RAY LINES
1.02	1126.	NA KA1. NA KA2. NA KB1. ZN LA1. ZN LA2. ZN LB1. IN LG1. PH MA1. PH MA2. PH MB .
1.24	839.	MG KA1. MG KA2. AS LA1. AS LA2. TB MA1. TB MA2. TB MB .
1.73	84790.	SI KA1. SI KA2. RB LA1. RB LA2. RB LB1. RB LB2. TA MA1. U MA1. TA MA2. U MA2.
2.05	68497.	P KA1. P KA2. <u>ZR LA1.</u> <u>ZR LA2.</u> PT MA1. PT MA2. AT MZ1.
2.53	470.	<u>RU LA1.</u> <u>RU LA2.</u> PD MA1. PD MA2. AT MA2.
3.70	17326.	<u>CA KA1.</u> <u>CA KA2.</u>
4.02	2097.	<u>CA KB1.</u>
4.55	371.	<u>TI KA1.</u>
6.30	157.	TB LA1. TB LN .
7.92	608.	<u>HF LA1.</u>
9.03	360.	<u>HF LB1.</u> HF LB2.
15.72	8006.	<u>ZR KA2.</u>
17.61	1221.	<u>ZR KB3.</u>

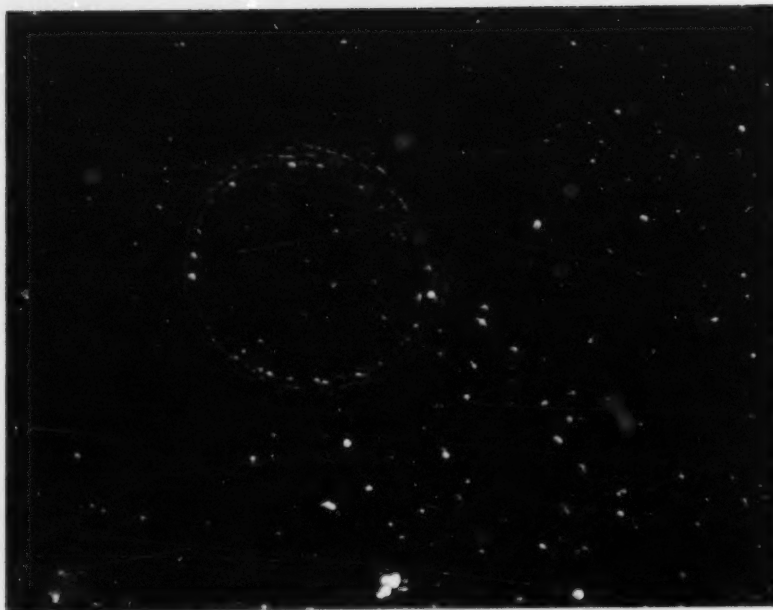
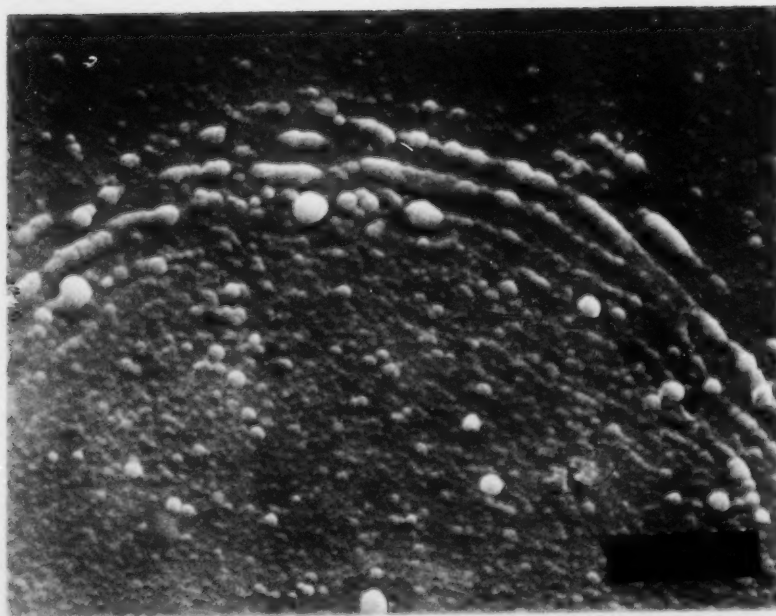


Figure H3

Electron Micrograph of
Circular Patterns on
 ZrO_2 Coatings.

a.



b.

Figure H4

Electron Micrograph of Fracture Surface of
 ZrO_2 Coated Glass (Sample #383)

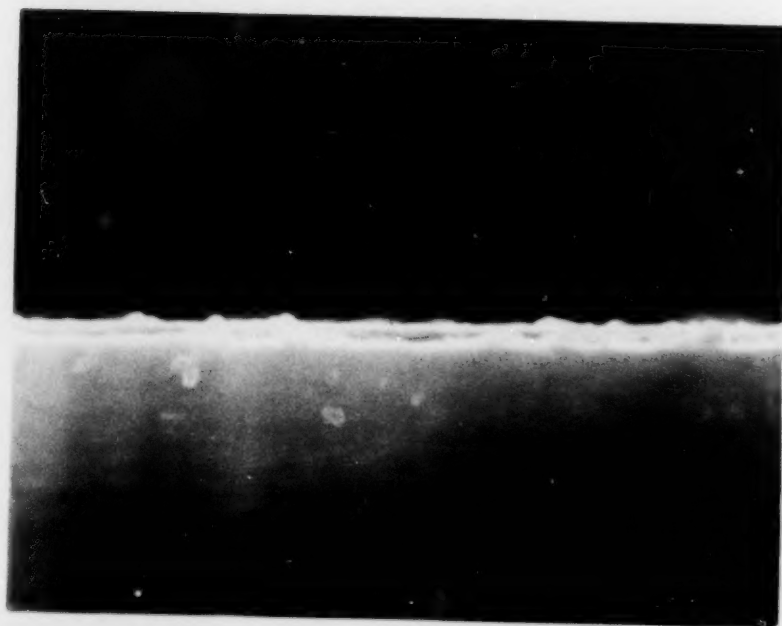


Figure H5

E.D. X-Ray Spectra

Job Number 83598 Date June 20/83

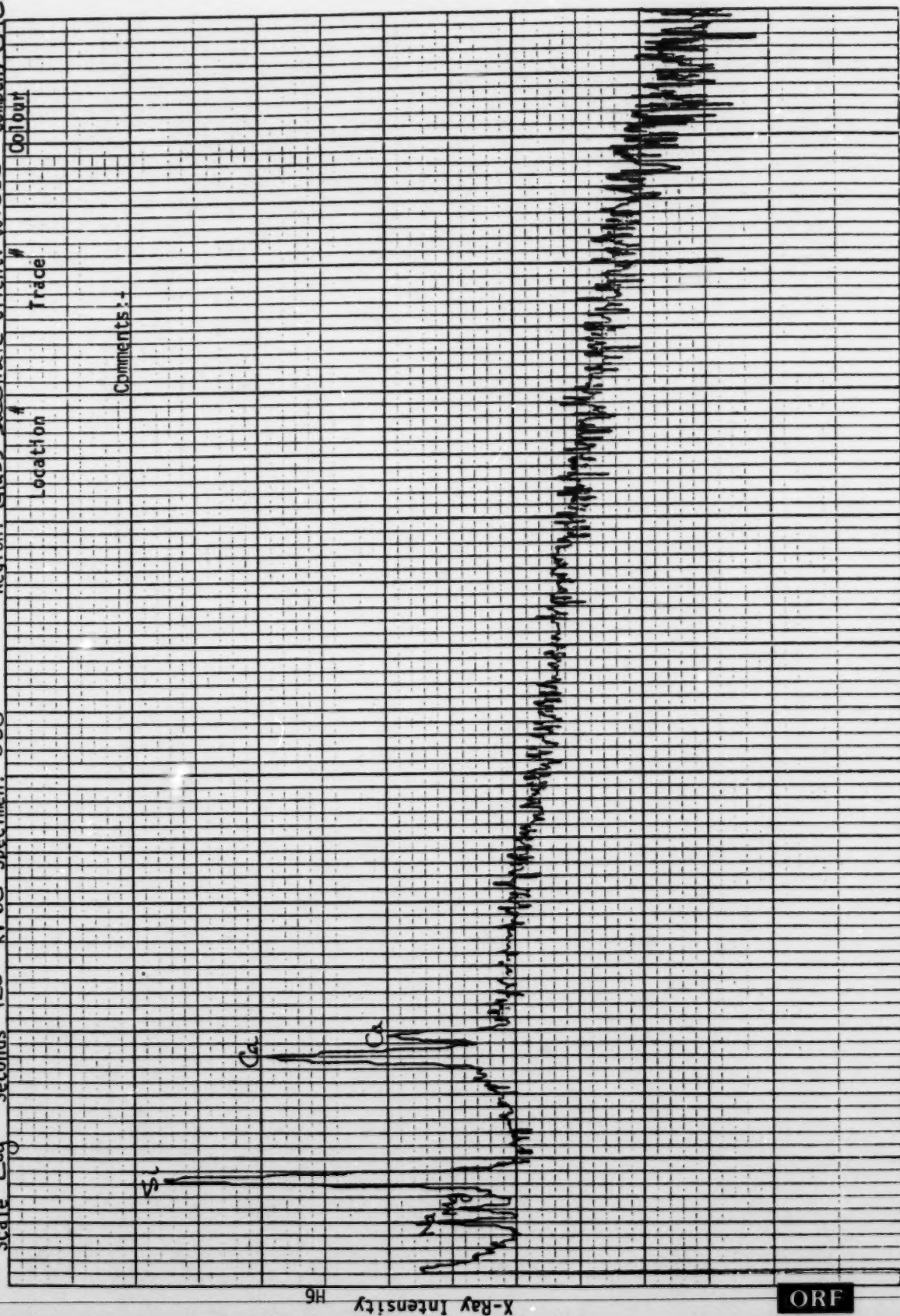
Scale Log Seconds 120 KV 30 Specimen: 383

Region: Glass substrate Client: W. Sze Company GTC.

Location

Trace

Comments:-



X-Ray Energy (keV)

Figure H6

E.D. X-Ray Spectra

Job Number 83598 Date June 20/83

Region: "Coated edge" Client: W. Sze Company G+C.

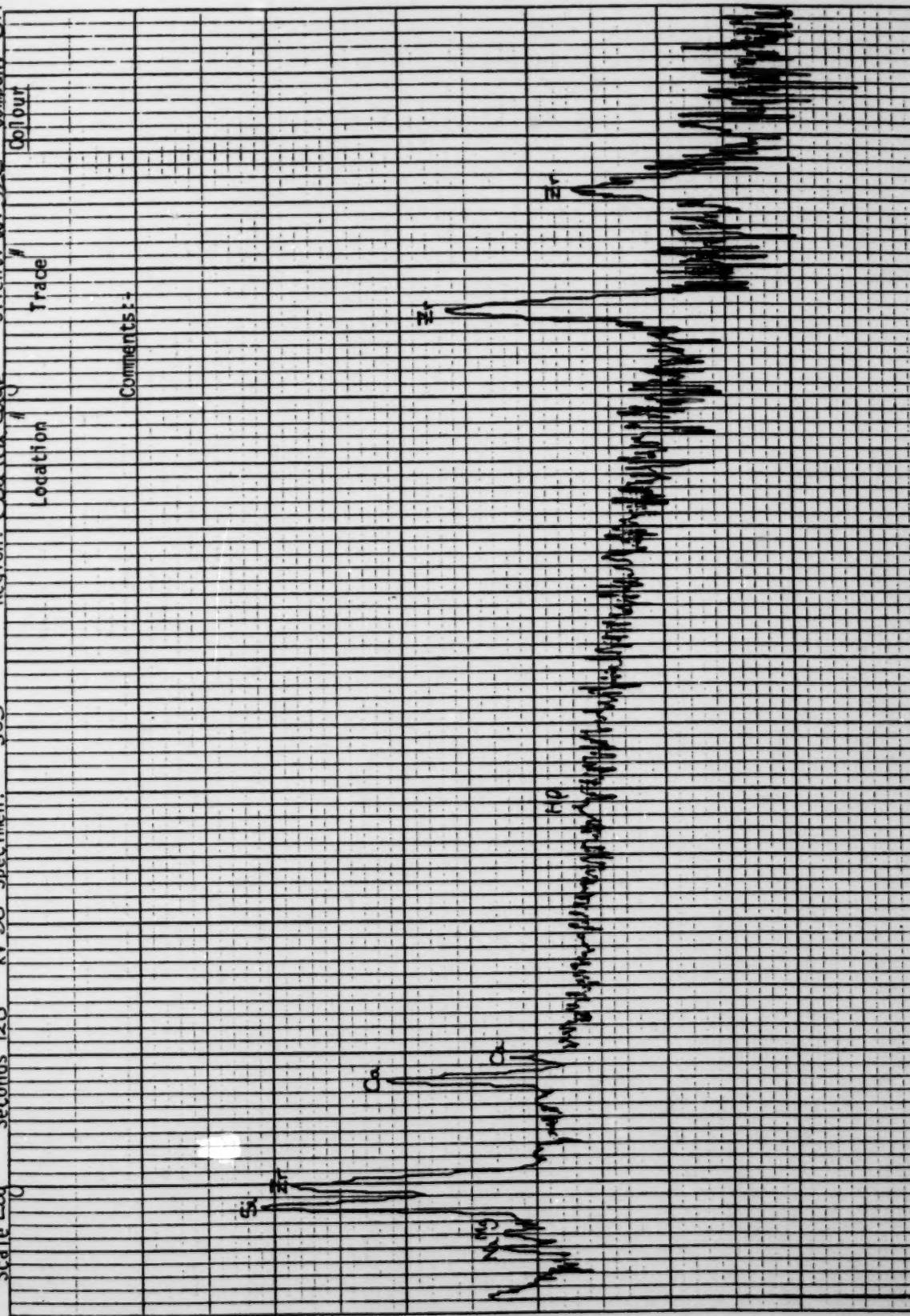
383

Specimen:

120

Seconds

Scale Log



Location Trace Colour

Comments: +

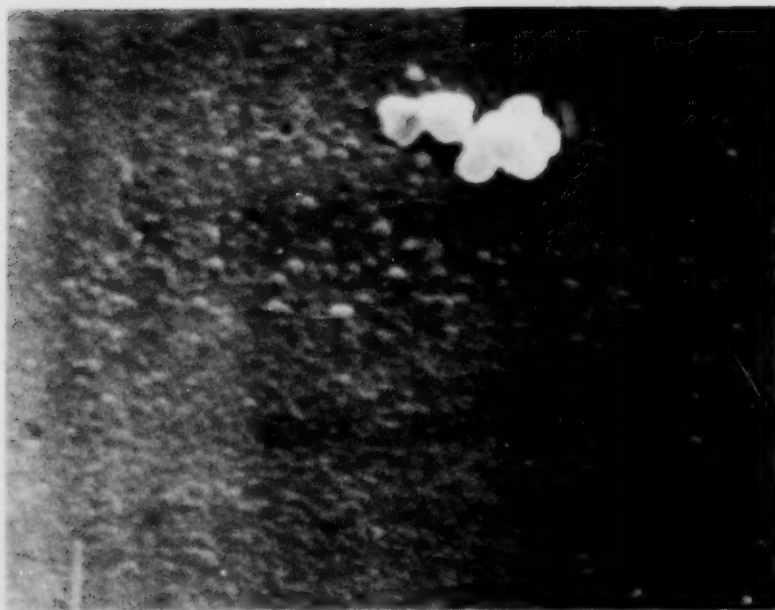
X-Ray Energy (keV)



Figure H7

Electron Micrographs of
 ZrO_2 Coatings on Window
Glass Substrate.

a.



b.

Figure H8

Electron Micrograph of ZrO_2 Coatings on a Window
Glass Substrate showing Hairline Cracks.

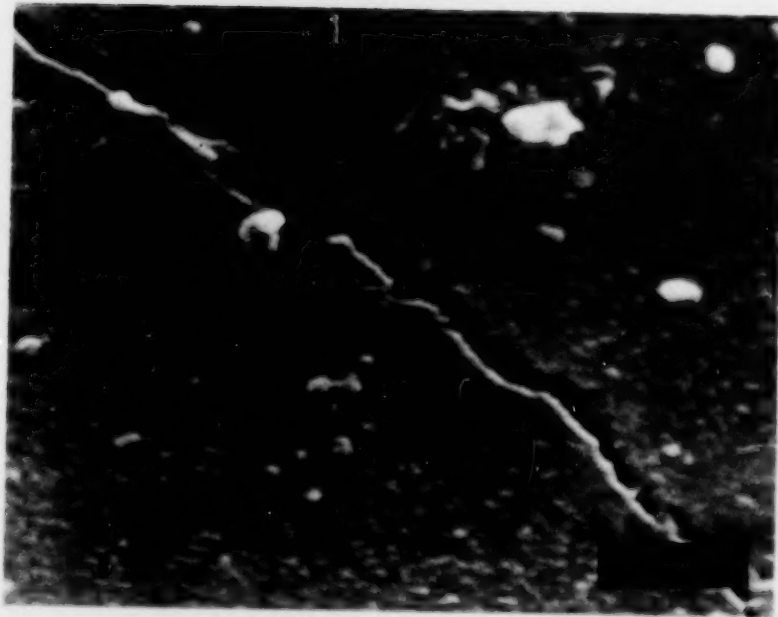


Figure H9

E.D. X-Ray Spectra

Job Number 83598 Date June 17/83

Scale Log Seconds 180 kV 30 Specimen: 432 Client: W. Sz Company G+C.

Location

Trade

Comments: -

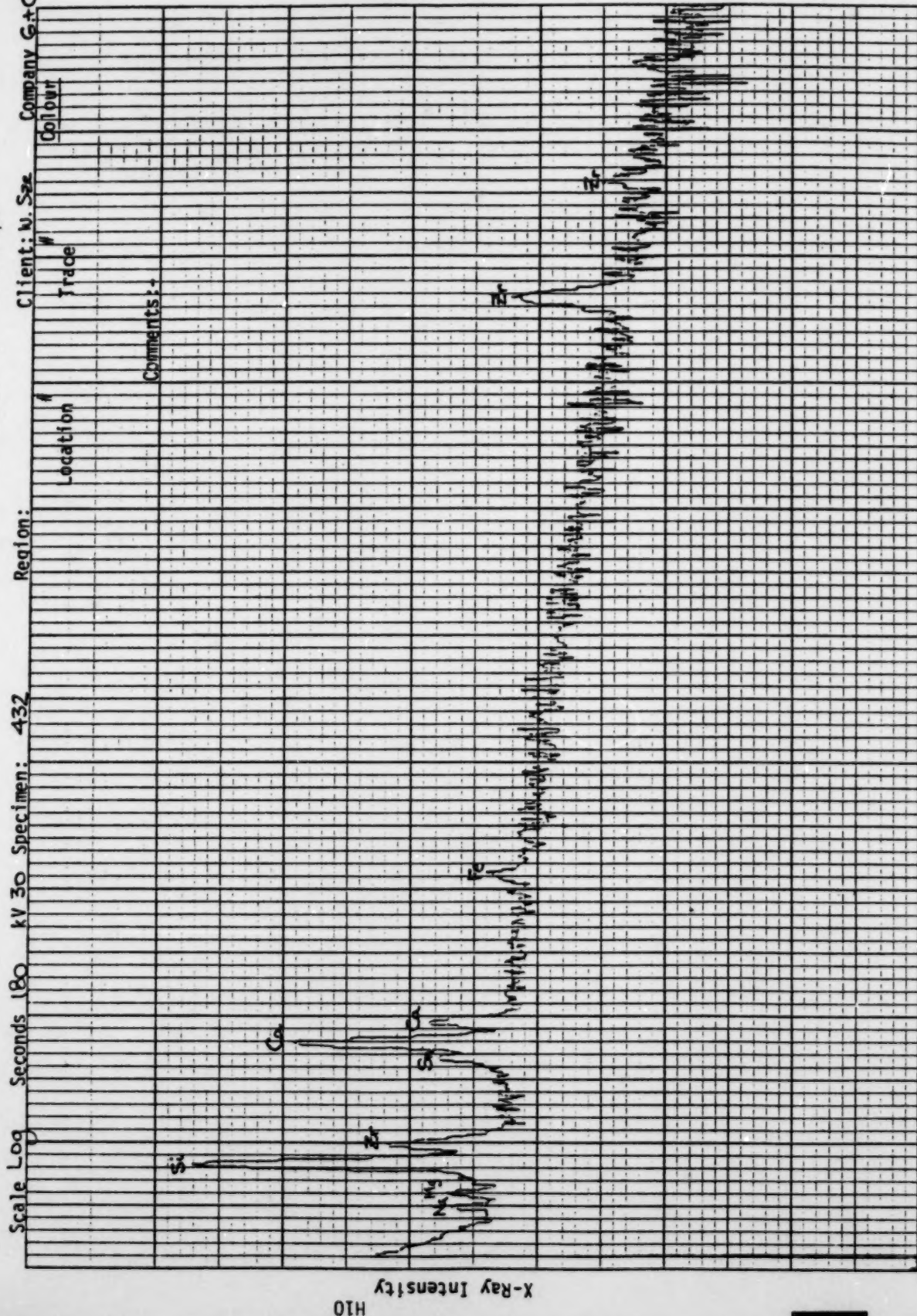


Figure H9 (b)

DATE 1-1-83

SPECTRUM 33598 432

ENERGY	COUNTS	X-RAY LINES
1.02	789.	NA KA1. NA KA2. NA KB1. ZN LA1. ZN LA2. ZN LB1. ZN LG1. PM HA1. PM MA2. PM MB.
1.24	886.	MG KA1. MG KA2. AS LA1. AS LA2. TB MA1. TB MA2. TB MB.
1.73	61498.	SI KA1. SI KA2. RB LA1. RB LA2. RB LB1. RB LB2. TA HA1. U HA1. TA MA2. U MA2.
2.06	3621.	ZR LA1. ZR LA2. PT HA1. PT MA2.
3.43	797.	SN LA1. SN LA2.
3.70	16814.	CA KA1. CA KA2. SN LB1. SN LB3.
4.02	1971.	CA KB1.
6.41	587.	FE KA1. FE KA2.
15.73	775.	ZR KA1.

Energy

energy conservation programs and analyses, thermal insulation design and evaluation, waste heat recovery, building energy systems and monitoring, heat storage systems and materials, thermoelectric generation, combustion technology, burner development, heat transfer analysis, solar systems monitoring, National Solar Test Facility, solar technology, wind power, coal, lignite and oil sands processing, alternate fuel utilization, battery and fuel cell technology, peat processing and utilization, fenestration measurements, heat pump development and test facilities, residential heating systems, air to air heat exchange test facility, photovoltaic devices, . . .

Environment

ambient air quality assessment, environmental impact assessments, long-range transport of atmospheric pollutants, precipitation chemistry, particulate characterization studies, emission inventories, source sampling, odour emission and control, asbestos measurement and control, occupational health and safety studies, diesel emission control technology, air pollution control, pesticide residues, trace metal analysis, trace organic analysis, radionuclide analysis, mutagenic testing, noise and vibration analysis, radiation measurements, particulate identification and measurement, water surveys, water purification, industrial and municipal wastewater treatment, membrane separation techniques, wet oxidation, solid waste treatment and recovery, hazardous waste treatment and disposal, indoor air quality assessments, priority pollutant analysis, landfill technology, . . .

Materials

building materials, plastics, composites, metals, glass and ceramics, wood and wood composites, biomaterials, adhesives and printing inks, fibres, yarns, fabrics and geotextiles, leather, organic and inorganic chemicals, specification development, quality assurance, mechanical, chemical and thermal properties, test method development, failure analysis, fire and flammability, glass-metal seals, metal and alloy powders, metallography, materials characterization, materials characterization by optical and electron microscopy and X-ray microanalysis, photovoltaic materials, materials corrosion resource centre, corrosion properties and control, bacterial corrosion, coatings and sealants, rubber technology, X-ray analysis, cement and concrete, soils and aggregates, gypsum, body armour testing, footwear, paper-making materials, roofing and waterproofing, waste material stabilization and solidification, . . .

Products & Processes

clothing, footwear and industrial textile products, knitting technology, thin and thick film systems, microelectronics development, fibre optics, instrumentation, bioengineering, ultrasonic and fluid shear devices, microwave drying, transportation and equipment testing, mathematical stress and vibration analysis, product, equipment and machinery design & development, fuel emulsification, organic analysis and characterization, chemistry of foodstuffs, pulp and paper processes, ceramics processing, metallurgical process development, powder metal technology, packaging applications, technical and economic evaluations, industrial engineering applications, process control, enzyme analysis, electrical testing, radioactive surveys, industrial microbiology, biotechnology, technical and management skills development seminars, paper products, absorbent consumer products, detergent and cosmetic formulation, metal chemical analysis, flash hydropyrolysis of coal, electroplating, . . .

Resources

mineral processing, hydro and pyrometallurgical processing of ferrous and non-ferrous ores, coal evaluation, coal ash utilization and product development, asbestos processing and applications, non-metallic minerals/industrial minerals processing and utilization, uranium processing, forest utilization, utilization of forest and agricultural wastes, utilization of industrial, mining and domestic wastes, energy and chemicals from biomass, in-plant waste reduction, mineralogical services, mining and metallurgical waste disposal, . . .

